PHYSICAL REVIEW E **95**, 012501 (2017)

Statistical model of a flexible inextensible polymer chain: The effect of kinetic energy

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(Received 19 October 2016; revised manuscript received 27 November 2016; published 3 January 2017)

Because of the holonomic constraints, the kinetic energy contribution in the partition function of an inextensible polymer chain is difficult to find, and it has been systematically ignored. We present the first thermodynamic calculation incorporating the kinetic energy of an inextensible polymer chain with the bending energy. To explore the effect of the translation-rotation degrees of freedom, we propose and solve a statistical model of a fully flexible chain of $N + 1$ linked beads which, in the limit of smooth bending, is equivalent to the well-known wormlike chain model. The partition function with the kinetic and bending energies and correlations between orientations of any pair of links and velocities of any pair of beads are found. This solution is precise in the limits of small and large rigidity-to-temperature ratio b/T. The last exact solution is essential as even very "harmless" approximation results in loss of the important effects when the chain is very rigid. For very high b/T, the orientations of different links become fully correlated. Nevertheless, the chain does not go over into a hard rod even in the limit $b/T \to \infty$: While the velocity correlation length diverges, the correlations themselves remain weak and tend to the value $\propto T/(N+1)$. The N dependence of the partition function is essentially determined by the kinetic energy contribution. We demonstrate that to obtain the correct energy and entropy in a constrained system, the T derivative of the partition function has to be applied before integration over the constraint-setting variable.

DOI: 10.1103/PhysRevE.95.012501

I. INTRODUCTION

Many real linear supramolecular assemblies, such as linear polymer macromolecules [1] and different aggregates [2–4], are inextensible. For this reason, the model of an inextensible chain is one of the basic models of the physics of polymers. However, the inextensibility expressed as a fixed length of chain's segments results in holonomic constrains in the chain partition function, which give rise to considerable mathematical difficulties in the related calculations [1,5,6]. In particular, because of these constraints the orientations and velocities of chain segments are not independent.

We used to enjoy the fact that the kinetic energy contribution to partition functions of different systems can be easily calculated and fully factorizes, and the statistical mechanical description reduces to finding the configurational partition function. This is not so in the case of an inextensible chain. The integration over translational and rotational degrees of freedom of such a chain in a thermal bath is a difficult problem as velocities of its different segments are not independent and the kinetic energy depends on the chain's flexibility. This is probably the main reason why the kinetic energy contribution in the partition function of an inextensible chain has been systematically ignored. To our knowledge, the only calculation of thermodynamical quantities of an inextensible chain, which incorporated the kinetic energy, was performed by Edwards and Goodyear [5] for a freely hinged chain. To deal with the constraints, these authors developed an elegant method which allowed them to calculate the free energy and velocity correlations for different beads. According to the authors, the power of their method lies in the fact that it avoids difficult integrals containing δ functions fixing the constraints. The problem, however, is that this method works only in the case of a freely hinged chain when the potential energy of its bending is zero. Moreover, in [5] the velocity correlation function was calculated after the discrete chain was represented by its continuous limit, and it is not clear how different the results for the actual and continuous model can be.

Incorporating the kinetic energy in the thermodynamics of an inextensible chain with arbitrarily strong bending energy is a challenging problem of a general physical interest. One aspect of this interest is to resolve the difficulty of dealing with the constraint-fixing δ functions which, in addition, can suggest a proper mathematical device for other constrained systems. Another interesting question is related to the velocity correlations and is as follows. One expects that for a very high chain rigidity the orientations of segments are highly correlated and they tend to align along a single direction. The question is if the velocities of different beads also strongly correlate in this limit, for, if yes, then, in this limit, a flexible chain goes over into a rigid rod. At last, a more practical aspect is that the kinetic energy contribution to the partition function of chain can have a substantial dependence on its total length N. This dependence is necessary for finding length distribution (polydispersity) in living polymers and aggregates reversibly self-assembling in solvents or melts of monomers. Particularly important is the question if this dependence contains terms of the form N^q: It was recently shown in [7,8] that the exponent q determines the power law dependence of the polydispersity on the monomer concentration.

In this paper we address the general case when a chain is discrete and has an arbitrary strong bending energy. It is important to realize that the coarse-grained description based on the idea of a smooth bending over the effective length scale comprising more than one real segment [9] is not applicable for our task as each of this individual segments has its own velocity and kinetic energy and must explicitly enter the theory. Thus, we have to consider a fully flexible chain where bending angles between neighboring segments are not restricted to small values. Therefore, we introduce a model of such chain

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which is equivalent to the well-known wormlike model if the bending is smooth. The chain consists of $N+1$ beads of mass M connected by rigid links of a fixed length. The constraints are fixed by the appropriate δ functions so that the form of the partition function is similar to that of Ref. [5]. The difference is in our explicit representation of these δ functions as integrals over auxiliary variables ξ and in the Hamiltonian of our model which has bending energy in the form of a cosine of the angle between two neighboring segments. The chain rigidity b enters the theory as a coefficient of the bending energy and can range from zero (freely hinged chain) to infinity (apparently rigid rod). The partition function of the model, the orientation correlations for any pair of segments, and velocity correlations for any pair of beads are found in the limits of a small rigidity-to-temperature ratio b/T and of very large b/T, and the obtained solution interpolates between these two precisely solvable cases. When b/T ranges from 0 to ∞, the mean cosine $\langle\cos\theta\rangle$ between the neighboring segments changes from 0 to 1. The orientational correlations depend only on the distance n-m between the segments n and m, and as $\langle\cos\theta\rangle$ goes to unity their correlation length logarithmically diverges while their values tend to 1. In contrast, the momentum correlations depend on the positions m and n of the beads with respect to the chain ends (or center). At the same time, in the limit $b/T\to\infty$ when $\langle\cos\theta\rangle\to 1$, the momentum correlations tend to the small value $TM/(N+1)$ independent of the beads' positions, indicating that the momentum correlation length diverges. Thus, the chain does not become a really hard rod even in the limit of infinite rigidity: Although the links' orientations are fully correlated and the chain has a practically straight rigid backbone, and although the momentum correlation length diverges, the momentum correlations remain weak. One may call this state a rigid chain or quasihard rod which possesses both individual and collective degrees of freedom. The energy of such a rigid chain is that of 2 degrees of freedom per each of $N+1$ beads plus 1 collective degree of freedom of the solid motion along the hard rod's backbone. Moreover, the partition function in this limit gets an N dependence of the form N^q signaling of a collective behavior and nontrivial power laws in the polydispersity dependence on the monomer concentration in case such chains are self-assembling from the melts or solutions [7,8]. This and other N-dependent terms in the partition functions are the effect of the kinetic energy, which shows that the translation-rotation degrees of freedom of polymer chains are indispensable in certain situations as their contribution to the N dependence of the thermodynamic quantities dominates. In the opposite limit of a very small b/T, the result is also nontrivial: The energy per bead is that of 2.57 conventional harmonic degrees of freedom, i.e., due to correlations between neighboring segments making an average angle $\pi/2$, the pointlike beads are neither three- nor exactly two-dimensional systems. The above energy is obtained by the T differentiating the partition function functional *before* integration over the constraint-setting auxiliary variable ξ. This operation order gives a correct result as it is equivalent to the definition of the average energy. In contrast, the differentiation of the partition function *after* the integral over ξ has been performed gives the energy of two degrees of freedom per bead, in which the correlations are missing. We conclude that, in a system with constraints imposed by some integral over an auxiliary variable ξ, the differentiation with respect to the parameters has to be performed before the ξ integration. Thus, in systems with unresolved constraints the partition function is a generating functional rather than just a function of the thermodynamical variables.

In the next Sec. II we introduce the model, formulate its partition function integral and solve it for large b/T. In Sec. III we found the orientation and momentum correlations. That the T differentiation and ξ integration cannot be permuted is demonstrated in Sec. IV. Section V concludes the paper with a brief account of the results. In the Appendix, which is an important integral part of the paper, the case of a small b/T is considered individually.

II. THE MODEL AND ITS PARTITION FUNCTION

A. The statistical integral of the model

The model chain consists of $N+1$ beads of mass M connected by N segments of length l. The Cartesian coordinates and conjugate momenta of the beads are, respectively, $\mathbf{r}_i$ and $\mathbf{p}_k$, $i=1,2,\dots,N+1$. The inextensibility imposes N obvious constraints on the coordinates,

$$|\mathbf{r}_{i+1}-\mathbf{r}_i| = l, \quad i=1,\dots,N, \tag{1}$$

thus restricting the number of the independent degrees of freedom from $3N+3$ to $3N+3-N=2N+3$. As shown in [5], the constraints also imply certain relations between the beads' momenta. To find them, we introduce unit vectors $\mathbf{t}_i$, indicating the segment orientations:

$$\frac{\mathbf{r}_{i+1}-\mathbf{r}_i}{l} = \mathbf{t}_i, \quad i=1,\dots,N. \tag{2}$$

The time derivative of $\mathbf{t}_i$ is

$$\dot{\mathbf{t}}_i = \frac{\mathbf{p}_{i+1}-\mathbf{p}_i}{Ml}. \tag{3}$$

However, an arbitrary change of a unit vector is its rotation, $\dot{\mathbf{t}}_i = [\omega\times\mathbf{t}_i]$. To get rid of the angular velocity ω, this equation is multiplied by $\mathbf{t}_i$, which gives the following N relation between the momenta and orientations:

$$(\mathbf{p}_{i+1}-\mathbf{p}_i)(\mathbf{r}_{i+1}-\mathbf{r}_i) = 0, \quad i=1,2,\dots,N. \tag{4}$$

The Hamiltonian of the model has the form

$$H = E_{\text{kin}} + U = \sum_{i=1}^{N+1}\frac{\mathbf{p}_i^2}{2M} - \frac{b}{2}\sum_{i=1}^{N-1}\mathbf{t}_i\mathbf{t}_{i+1}. \tag{5}$$

The angle θ_{i+1} between the neighbor segments $\mathbf{t}_{i+1}$ and $\mathbf{t}_i$ ranges from 0 to π and the bending energy scales as $b\mathbf{t}_i\mathbf{t}_{i+1} = b\cos\theta_{i+1}$. This potential energy U favors parallel alignment of segments and is a direct generalization of that of the wormlike model for arbitrary bending angles, which is seen from the following formulas:

$$\frac{\lambda_{\text{worm}}}{2}\int_o^{L_c} dl\left|\frac{d\mathbf{t}}{dl}\right|^2 = \frac{\lambda_{\text{worm}}}{2}\lim_{l\to 0}\sum_{i=1}^{N-1} l\,\frac{(\mathbf{t}_{i+1}-\mathbf{t}_i)^2}{l^2}$$

$$\to -\frac{b}{2}\sum_{i=1}^{N-1}(\mathbf{t}_i\mathbf{t}_{i+1}-1). \tag{6}$$

The rigidity (bending) constant b of our model, which can range from 0 to ∞, is related to λ_{worm} as $b = 2\lambda_{\text{worm}}/l$.

We introduce the notation $\mathcal{D}x^N = dx_1 dx_2 \cdots dx_N$ for the N-dimensional integration measure in a variable x. Then the canonical partition function of the model which accounts for the constrains (1) and (4) is

$$Z = \frac{1}{(2\pi\hbar)^{2N+3}} \int \mathcal{D}\mathbf{r}^{N+1}\mathcal{D}\mathbf{p}^{N+1} \prod_{i=1}^{N} \times \delta\left[\frac{(\mathbf{p}_{i+1}-\mathbf{p}_i)(\mathbf{r}_{i+1}-\mathbf{r}_i)}{l}\right]\delta(|\mathbf{r}_{i+1}-\mathbf{r}_i|-l)e^{-\beta H}. \tag{7}$$

Here the factor $1/(2\pi\hbar)^{2N+3}$ corresponds to the $2N+3$ quasiclassical degrees of freedom, $\beta = 1/T$, where T is the temperature (in units of energy). The arguments of the δ functions are chosen as to get the correct dimensionality $[1/\mathbf{pr}]$ per each cancelled degree of freedom. Except for this constant factor and the form of H, this Z coincides with the partition function of a freely hinged chain of Ref. [5]. The δ functions make this integral difficult, and Edwards and Goodyear avoided the direct integration even in the case of a freely hinged chain [5]. By contrast, we will deal with the integral (7) directly. To this end we change from the variables $\mathbf{r}_i$ to $\mathbf{t}_i$ and take the δ functions in the analytical form.

We first change from the variables $\mathbf{r}_i$ to the variables $(\mathbf{r}_1, \mathbf{r}_2-\mathbf{r}_1, \mathbf{r}_3-\mathbf{r}_2, \ldots, \mathbf{r}_{N+1}-\mathbf{r}_N)$; the Jacobian of this transformation is 1. Integration over the external coordinate $\mathbf{r}_1$ gives the volume V. The other integrals over $(\mathbf{r}_{i+1}-\mathbf{r}_i)$ are straightforward and, due to $\delta(|\mathbf{r}_{i+1}-\mathbf{r}_i|-l)$, reduce to the integration over the solid angles $d^2\mathbf{t}_i$:

$$\delta(|\mathbf{r}_{i+1}-\mathbf{r}_i|-l)|\mathbf{r}_{i+1}-\mathbf{r}_i|^2 d|\mathbf{r}_{i+1}-\mathbf{r}_i| d^2\mathbf{t}_i \to l^2 d^2\mathbf{t}_i. \tag{8}$$

For each segment $\mathbf{t}_i$ we choose a local spherical reference frame O_i with the polar axis along $\mathbf{t}_i$ and introduce the azimuthal angle ϕ_{i+1} so that the vector of next neighbor segment in O_i is $\mathbf{t}_{i+1} = (1,\theta_{i+1},\phi_{i+1})$. The Jacobian of the transformation to the local reference frame is 1 and the element of the solid angle has the form

$$d^2\mathbf{t}_i = \sin\theta_{i+1} d\theta_{i+1} d\phi_{i+1}. \tag{9}$$

The δ functions are taken in the standard representation,

$$\delta[(\mathbf{p}_{i+1}-\mathbf{p}_i)\mathbf{t}_i] = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\xi_i' e^{i(\mathbf{p}_{i+1}-\mathbf{p}_i)\mathbf{t}_i\xi_i'}. \tag{10}$$

Changing from the variables ξ_i' to $\xi_i = \sqrt{M/\beta}\xi_i'$, the partition function can be reduced to the following integral:

$$Z = \frac{l^{2N}V(\beta/M)^{N/2}}{(2\pi)^N(2\pi\hbar)^{2N+3}} \int \mathcal{D}\mathbf{t}^N \mathcal{D}\mathbf{p}^{N+1} e^{-\beta H} \int \mathcal{D}\xi^N \times \exp\left[\sqrt{\beta/M}\sum_{i=1}^{N} i(\mathbf{p}_{i+1}-\mathbf{p}_i)\mathbf{t}_i\xi_i\right]. \tag{11}$$

The next step is simple but very important. We regroup the last sum in the above Z to get the form linear in $\mathbf{p}$:

$$i\sum_{i=1}^{N}(\mathbf{p}_{i+1}-\mathbf{p}_i)\mathbf{t}_i\xi_i' = \sum_{i=1}^{N+1}\mathbf{b}_i\mathbf{p}_i, \tag{12}$$

$$\mathbf{b}_i = \begin{cases} -i\mathbf{t}_1\xi_1, & i = 1, \\ i(\mathbf{t}_{i-1}\xi_{i-1} - \mathbf{t}_i\xi_i), & i = 2,\ldots,N, \\ i\mathbf{t}_N\xi_N, & i = N+1. \end{cases} \tag{13}$$

Now the integration over the momenta factorizes into $N+1$ Gaussian integrals:

$$I_p = \int \mathcal{D}\mathbf{p}^{N+1} \exp\sum_{i=1}^{N+1}\left(-\frac{\beta}{2M}\mathbf{p}_i^2 + \sqrt{\beta/M}\mathbf{b}_i\mathbf{p}_i\right) = (2\pi)^{\frac{3(N+1)}{2}}(\beta/M)^{-N-3/2}\exp\left(\frac{1}{2}\sum_{i=1}^{N+1}\mathbf{b}_i^2\right). \tag{14}$$

Making use of this result in the partition function (11) and substituting expression (13) for $\mathbf{b}_i$, after some algebra we arrive at the following formula:

$$Z = \text{const}\int \mathcal{D}\xi^N \exp\left(-\sum_{k=1}^{N}\xi_k^2\right)\int \mathcal{D}\mathbf{t}^N \exp\sum_{i=1}^{N-1} a_i(\mathbf{t}_i\mathbf{t}_{i+1}). \tag{15}$$

Here

$$a_i = \lambda + \xi_i\xi_{i+1}, \quad i = 1,\ldots,N-1, \tag{16}$$

where $\lambda = \beta b/2$ is the main parameter of the model, the effective temperature-dependent rigidity. The constant factor in (15) is

$$\text{const} = \frac{l^{2N}V\left(\frac{\beta}{m}\right)^{-N-3/2}}{(2\pi\hbar^2)^{N+3/2}}. \tag{17}$$

The integral over $\mathcal{D}\mathbf{t}^N$ factorizes into N integrals over $d\theta_i d\phi_i$. The first link is randomly oriented, $\int d^2\mathbf{t}_1 = 4\pi$. Then, in the context of Eq. (9), one has

$$\int \mathcal{D}\mathbf{t}^N \exp\sum_{i=1}^{N-1} a_i(\mathbf{t}_j\mathbf{t}_{j+1}) = 4\pi\prod_{i=1}^{N-1}\int_0^{2\pi} d\phi_{i+1}\int_0^{\pi} d\theta_{i+1}\sin\theta_{i+1}\exp(a_i\cos\theta_{i+1}) = (2\pi)^N 2^N \prod_{i=1}^{N-1}\frac{\sinh a_i}{a_i}. \tag{18}$$

After the $\mathbf{t}$ integration the remaining task is to solve the integral $Z = \text{const}(4\pi)^N Z'$, where

$$Z' = \int \mathcal{D}\xi^N \exp\left(-\sum_{k=1}^{N}\xi_k^2\right)\prod_{i=1}^{N-1}\frac{\sinh a_i}{a_i}. \tag{19}$$

We rewrite Z' in the exponential form

$$Z' = \int \mathcal{D}\xi^N e^S, \tag{20}$$

where

$$S(\xi) = \sum_{i=1}^{N-1}\left(-\xi_i^2 + \ln\sinh a_i - \ln a_i\right) - \xi_N^2. \tag{21}$$

For any λ the function $S(\xi)$ has a maximum at the point $\xi_i = 0, i = 1,2,\dots,N$. The Taylor expansion about this point is

$$S = S(0) - \frac{1}{2}\sum_{i,j=i,i\pm1} S_{ij}\xi_i\xi_j + R, \tag{22}$$

where

$$S(0) = (N-1)\ln\frac{\sinh\lambda}{\lambda}, \tag{23}$$

S_{ij} is the matrix of the second derivatives $S_{ij} = -(\partial^2 S/\partial\xi_i\partial\xi_j)$, and R is the sum of all the higher-order terms, taken at $\xi = 0$. The series R has the form

$$R = \sum_{n=2}^{\infty}\frac{(-1)^{n+1}}{n}\left[\frac{1}{\sinh^n\lambda} - \frac{1}{\lambda^n}\right]\sum_{i=1}^{N-1}(\xi_i\xi_{i+1})^{2n}. \tag{24}$$

The matrix S_{ij} consists of the following elements:

$$\begin{aligned} &S_{i,i} = 2, \quad i = 1,2,\dots,N,\\ &S_{i,i+1} = S_{i+1,i} = -C = -\left(\coth\lambda - \frac{1}{\lambda}\right),\\ &\quad i = 1,2,\dots,N-1,\\ &S_{i,j} = 0, \quad j \neq i-1,i,i+1. \end{aligned} \tag{25}$$

For large λ, the terms on the order ξ^{2n} in R behave as λ^{-n}, the expression in the square brackets vanishes for all $n \geqslant 1$, and the expansion reduces to the quadratic terms. Thus, S determined by the matrix S_{ij} is exact in the limit $\lambda \to \infty$. We first consider the partition function in this limit.

B. Partition function in the limit of large λ

For large λ, in S (22) we retain only the quadratic terms determined by the matrix S_{ij} (25):

$$S \simeq S(0) - \frac{1}{2}\sum_{i,j=i,i\pm1} S_{ij}\xi_i\xi_j. \tag{26}$$

S_{ij} is a tridiagonal square $N \times N$ Toeplitz matrix as it has nonzero elements only on the three main diagonals, and at each diagonal they are all the same [10]. If its eigenvalues are positive, the integral Z' (20) in the Gaussian approximation (26) is equal to

$$Z' = \frac{(2\pi)^{\frac{N}{2}}\exp S(0)}{\sqrt{|\det S_{ij}|}}. \tag{27}$$

The eigenvalues μ_n of a tridiagonal Toeplitz matrix are known [10]. For the $N \times N$ matrix (25) they are given by the formula

$$\mu_n = 2 - 2C\cos\left(\frac{\pi n}{N+1}\right), \quad n = 1,\dots,N. \tag{28}$$

As required, these eigenvalues are positive since $0 \leqslant C < 1$ [Eq. (25)]. The determinant of S_{ij} is equal to the product of these eigenvalues:

$$\det S_{ij} = \prod_{n=1}^{N}\mu_n. \tag{29}$$

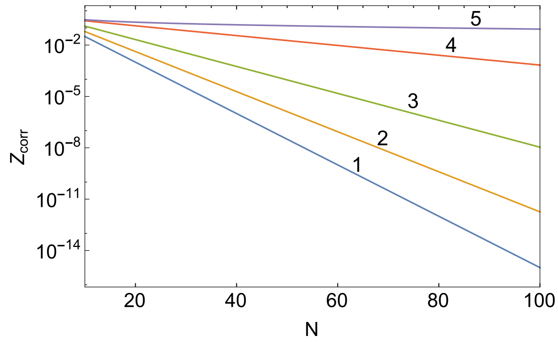

FIG. 1. The correlation partition function Z_{corr} vs chain length N for different C (mean $\cos\theta$): $C = 0.1$ (curve 1), $C = 0.7$ (2), $C = 0.9$ (3), $C = 0.99$ (4), and $C = 0.9999$ (5).

Finally, the partition function obtained can be presented as the product of three different contributions:

$$Z = Z_{\mathrm{conf}}Z_{\mathrm{kin}}Z_{\mathrm{corr}}. \tag{30}$$

Here Z_{conf} is the purely configurational integral (18) which has no contribution from the momenta:

$$Z_{\mathrm{conf}} = (4\pi)^N\left(\frac{\sinh\lambda}{\lambda}\right)^{N-1}. \tag{31}$$

The kinetic Z_{kin} is the integral over the momenta of the $2N+3$ independent degrees of freedom disregarding their correlations:

$$Z_{\mathrm{kin}} = \frac{Vl^{2N}}{(2\pi\hbar^2)^{N+3/2}}\left(\frac{\beta}{m}\right)^{-N-\frac{3}{2}} = \frac{Vl^{2N}}{\Lambda^{2N+3}}, \tag{32}$$

where Λ is the thermal de Broglie wavelength, $\Lambda = (\frac{2\pi\hbar^2}{mkT})^{\frac{1}{2}}$. At last, Z_{corr} is equal to$|\det S_{ij}|^{-1/2}$:

$$Z_{\mathrm{corr}} = \prod_{n=1}^{N}\left[2 - 2C(\lambda)\cos\left(\frac{n\pi}{N+1}\right)\right]^{-1/2}. \tag{33}$$

The determinant of the matrix S_{ij} appears as the result of integration over the variables ξ fixing the constraints (4). These constraints violate independence between the orientations and momenta so that Z_{corr} can be associated with the correlations. The correlation partition function Z_{corr}, which is one of the effects of the presence of momenta in the Hamiltonian, has a strong N dependence (Fig. 1). Due to this N dependence, Z_{corr} has a sharp dependence on C (Fig. 2), which is the nondiagonal element of the matrix S_{ij} (mean $\cos\theta$; see below), [Eq. (25)] and which monotonously increases with the rigidity λ (Fig. 3). For $C = 0$, $|\det S_{ij}(0)| = 2^N$, whereas for $C = 1$ it has a very different value $|\det S_{ij}(1)| = N+1$ [this can be proved by the induction method: $\Delta_1 = 2$; assume $\Delta_{N-1} = (-1)^{N-1}N$, then, making use of the known formula for the determinant of a tridiagonal matrix, one has $\Delta_N = -2(-1)^{N-1}N - (-1)^{N-2}(N-1) = (-1)^N(N+1)$]. Thus, the correlation partition function at the two extremes of C is

$$\begin{aligned} &Z_{\mathrm{corr}}(C=0) = 2^{-N/2},\\ &Z_{\mathrm{corr}}(C=1) = \frac{1}{\sqrt{N+1}}. \end{aligned} \tag{34}$$

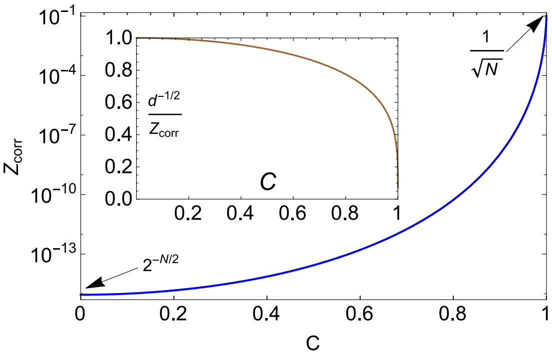

FIG. 2. The correlation partition function $Z_{\rm corr} = |\det S_{ij}|^{-1/2}$ vs mean cosine C. (Inset) Ratio $d^{-1/2}/Z_{\rm corr}$ of the approximate expression $1/d^{1/2}$, where d is computed by the formula (36), to the exact $Z_{\rm corr}$. $N = 100$.

The N dependence of Z is important in processes of chains' formation from monomers. Z_{conf} and $Z_{\rm kin}$ are normal in that they favor longer chains and more so for lower λ. By contrast, Figs. 1 and 2 show that $Z_{\rm corr}$ is larger for smaller N and higher λ and C, implying that its N dependence favors shorter chains and that for higher λ the aggregation numbers can be larger. Thus, correlations partially suppress the formation of long soft chains.

For large N the product (29) can be approximately converted to an integral:

$$\left|\det S_{ij}\right| = \exp \sum_{i=1}^{N} \ln|\mu_n|$$
$$\simeq \exp\left[\frac{N}{\pi}\int_0^{\pi} \ln(2 - 2C\cos x)dx\right]. \tag{35}$$

The integral in the second line is equal to $\pi \ln(1 + \sqrt{1 - C^2})$, and the approximate expression d for $\det S_{ij}$ is

$$|\det S_{ij}|(C) \simeq d(C) = (1 + \sqrt{1 - C^2})^N. \tag{36}$$

For $\lambda = C = 0$, both the exact and the approximate formulas for the determinant give the same value $|\det S_{ij}|(0) = d(0) = 2^N$. However, in the limit $\lambda \to \infty$, $C \to 1$, the approximate $d(1) = 1$ is very different from the exact value $N + 1$ (Fig. 2). The two formulas start to considerably deviate from one another as C is approaching 1. This shows that apparently harmless approximation of the product by the integral (the integration domain $[0,1]$ is partitioned into very small elements $1/N!$) is completely unacceptable when rigidity is large and a collective behavior, which manifests itself by the appearance of the collective quantity N in $Z_{\rm corr}$, takes the effect. We shall see that the velocity correlations also undergo a sharp change at $C \lessapprox 1$, which can be found only from the exact formulas.

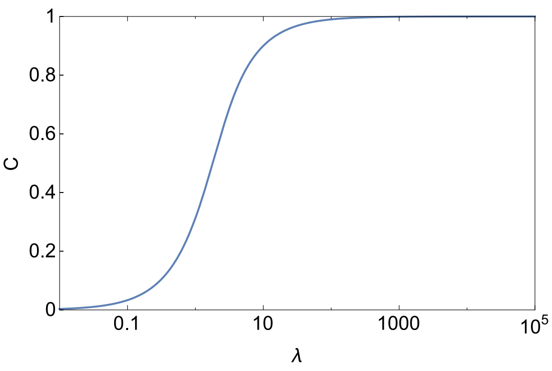

FIG. 3. The nondiagonal matrix element C, which at the same time is the mean cosine $\langle\cos\theta\rangle$ of the angle between neighboring links, as a function of the effective rigidity λ.

C. Partition function in the limit of small λ

The above formulas (30)–(33) were derived under the assumption of large λ. It turns out, however, that even for small λ their prediction is meaningful. The partition function and correlations for small λ are considered in the Appendix. It is an important integral part of this paper, but because the techniques used in the calculations for small λ are both substantially different from that for large λ and very extensive, we decided to separate them from the main text.

The result of Appendix shows that the partition function $\widetilde{Z}$ for small λ in its form is remarkably close to that obtained for very large λ if we set $C = 0$ in $Z_{\rm corr}$,

$$\widetilde{Z} = \widetilde{Z}_{\rm conf} Z_{\rm kin} Z_{\rm corr}(0), \tag{37}$$

where

$$\widetilde{Z}_{\rm conf} = (4\pi)^N \left(\frac{\sinh\lambda}{\lambda} + 0.06 + 0.02\lambda^2\right)^{N-1}, \tag{38}$$

which, for small λ, almost exactly coincides with $Z_{\rm conf}$. We see that $\widetilde{Z}(\lambda) \cong Z(\lambda \ll 1)$ so that Z given by the formulas (30)–(33) is a very good interpolation between large and small λ. Therefore, in what follows we will make use of these formulas for all λ, neglecting the very small corrections to $\sinh\lambda/\lambda$ in (38).

III. CORRELATIONS OF THE ORIENTATIONS AND MOMENTA

A. General formulas

In this section we find correlations $\langle \mathbf{p}_m \mathbf{p}_n\rangle$ between momenta of any pair of beads and correlations $\langle \mathbf{t}_m \mathbf{t}_n\rangle$ between any pair of segments. The velocity correlation $\langle \mathbf{v}_m \mathbf{v}_n\rangle$ is merely $\langle \mathbf{p}_m \mathbf{p}_n\rangle/M^2$. The quantities of our interest are

$$\langle \mathbf{p}_m \mathbf{p}_n\rangle = Z^{-1}\int \mathcal{D}\mathbf{t}^N \mathcal{D}\mathbf{p}^{N+1} \mathcal{D}\xi^N \mathbf{p}_m \mathbf{p}_n e^{-\beta H} \tag{39}$$

and

$$\langle \mathbf{t}_m \mathbf{t}_n\rangle = Z^{-1}\int \mathcal{D}\mathbf{t}^N \mathcal{D}\mathbf{p}^{N+1} \mathcal{D}\xi^N \mathbf{t}_m \mathbf{t}_n e^{-\beta H}. \tag{40}$$

Consider first $\langle \mathbf{p}_m \mathbf{p}_n\rangle$, which can be presented in the form

$$\langle \mathbf{p}_m \mathbf{p}_n\rangle = \int \mathcal{D}\mathbf{t}^N \mathcal{D}\xi_n^N e^{-\beta U} I_{p,mn}, \tag{41}$$

where

$$I_{p,mn} = Z^{-1}\int \mathcal{D}\mathbf{p}^{N+1}\mathbf{p}_m\mathbf{p}_n \times \exp\sum_{i=1}^{N+1}\left(-\frac{\beta}{2M}\mathbf{p}_i^2+\sqrt{\beta/M}\mathbf{b}_i\mathbf{p}_i\right). \tag{42}$$

This integral over momenta can be obtained from I_p (14) by differentiating with respect to the components of $\mathbf{b}$:

$$I_{p,mn} = \frac{\partial^2}{Z\partial\mathbf{b}_m\partial\mathbf{b}_n}I_p = \frac{M}{\beta}(3\delta_{mn}+\mathbf{b}_m\mathbf{b}_n I_p Z^{-1}). \tag{43}$$

Making use of this result and expression (13) for $\mathbf{b}$ in the definition (41) of $\langle\mathbf{p}_m\mathbf{p}_n\rangle$, one arrives at the formula

$$\langle\mathbf{p}_m\mathbf{p}_n\rangle = \frac{M}{\beta}(3\delta_{mn}-I_{m-1,n-1}-I_{mn}+I_{m-1,n}+I_{m,n-1}), \tag{44}$$

where

$$I_{mn} = Z^{-1}\int \mathcal{D}\xi^N\xi_m\xi_n\exp\left(-\sum_{k=1}^{N}\xi_k^2\right)\langle\cos\theta_{mn}\rangle_\xi, \tag{45}$$

$$\langle\cos\theta_{mn}\rangle_\xi = \int \mathcal{D}\mathbf{t}^N(\mathbf{t}_m\mathbf{t}_n)\exp\left(\sum_{i=1}^{N-1}a_i\mathbf{t}_i\mathbf{t}_{i+1}\right). \tag{46}$$

Due to the ξ dependence of the quantity a_i [Eq. (16)], $\langle\cos\theta_{mn}\rangle_\xi$ is the function of the variables ξ. The best way to find $\langle\cos\theta_{mn}\rangle_\xi$ is to resort to the argument by Landau and Lifshitz [11]. The cosine of the angle θ_{ac} between any links a and c is

$$\cos\theta_{ac} = \cos\theta_{ab}\cos\theta_{bc} - \sin\theta_{ab}\sin\theta_{bc}\cos\phi_{ab,bc}, \tag{47}$$

where link b is anywhere between a and c, and $\phi_{ab,bc}$ is the angle between the planes $(\mathbf{t}_a,\mathbf{t}_b)$ and $(\mathbf{t}_b,\mathbf{t}_c)$. Averaging this formula and bearing in mind that the planes ab and bc are independent, one obtains $\langle\cos\theta_{ac}\rangle_\xi = \langle\cos\theta_{ab}\rangle_\xi\langle\cos\theta_{bc}\rangle_\xi$. Then, in particular, $\langle\cos\theta_{14}\rangle_\xi = \langle\cos\theta_{13}\rangle_\xi\langle\cos\theta_{34}\rangle_\xi$, and, since $\langle\cos\theta_{13}\rangle_\xi = \langle\cos\theta_{12}\rangle_\xi\langle\cos\theta_{23}\rangle_\xi$, one gets $\langle\cos\theta_{14}\rangle_\xi = \langle\cos\theta_{12}\rangle_\xi\langle\cos\theta_{23}\rangle_\xi\langle\cos\theta_{34}\rangle_\xi$, and so on. Thus, for $n > m$,

$$\langle\cos\theta_{mn}\rangle_\xi = \langle\cos\theta_{m,m+1}\rangle_\xi\langle\cos\theta_{m+1,m+2}\rangle_\xi\cdots\langle\cos\theta_{n-1,n}\rangle_\xi. \tag{48}$$

The factor $\langle\cos\theta_{n,n+1}\rangle_\xi$ (46) is readily obtained:

$$\langle\cos\theta_{n,n+1}\rangle_\xi = (2\pi)2\left(\frac{\cosh a_n}{a_n}-\frac{\sinh a_n}{a_n^2}\right)\prod_{i\neq n}^{N-1}\frac{\sinh a_i}{a_i}. \tag{49}$$

Coming back to the integral (45), one has

$$I_{mn} = \frac{(4\pi)^N}{Z}\frac{M}{\beta}\int \mathcal{D}\xi^N\xi_m\xi_n\exp\left(-\sum_{k=1}^{N}\xi_k^2\right)\prod_{j=m,\dots,n-1} \times\left(\frac{\cosh a_j}{a_j}-\frac{\sinh a_j}{a_j^2}\right)\prod_{i\neq j}\frac{\sinh a_i}{a_i}. \tag{50}$$

Making use of formulas (46) and (49) in the definition (40), one also gets a formula for the general orientation correlator:

$$\langle\mathbf{t}_m\mathbf{t}_n\rangle = \frac{(4\pi)^N}{Z}\int \mathcal{D}\xi^N\exp\left(-\sum_{k=1}^{N}\xi_k^2\right)\prod_{j=m,\dots,n-1} \times\left(\frac{\cosh a_j}{a_j}-\frac{\sinh a_j}{a_j^2}\right)\prod_{i\neq j}\frac{\sinh a_i}{a_i}. \tag{51}$$

B. Correlations for large λ

The integral I_{mn} can be readily computed for large λ using a Gaussian approximation. In this case the factors $\coth a - 1/a$ do not change the quadratic form (25) as their second- and higher-order derivatives at $\xi_i = 0$ vanish in this limit. Then one has

$$I_{mn} = \frac{M}{\beta}C^{n-m}S_{mn}^{-1}, \tag{52}$$

where S_{mn}^{-1} is the element of the matrix inverse to S_{mn}. Similarly, one finds the mean $\cos\theta$ and the correlator $\langle\mathbf{t}_m\mathbf{t}_n\rangle$ (51) for large λ:

$$\langle\cos\theta\rangle = \frac{(2\pi)^N 2^N}{Z}\int \mathcal{D}\xi^N\langle\cos\theta_{n,n+1}\rangle_\xi = C, \tag{53}$$

$$\langle\mathbf{t}_m\mathbf{t}_n\rangle = \langle\cos\theta\rangle^{n-m} = C^{n-m}. \tag{54}$$

Now we proceed with the momentum correlations. Formula (44) with I_{mn} from (52) can be rewritten as follows:

$$\langle\mathbf{p}_m\mathbf{p}_n\rangle = \frac{3M}{\beta}\delta_{mn} + \frac{M}{\beta}C^{n-m}\big[-S_{mn}^{-1}-S_{m-1,n-1}^{-1} + CS_{m-1,n}^{-1}+C^{-1}S_{m,n-1}^{-1}\big]. \tag{55}$$

If $m = n$, $S_{m,n-1}^{-1}$ in the last term is replaced with $S_{n-1,m}^{-1}$; see Eq. (56). The inverse elements of a tridiagonal Toeplitz matrix of the form (25) were found by da Fonseca and Petronilho in [12]. For $n \geqslant m$, these are

$$S_{mn}^{-1} = S_{nm}^{-1} = (-1)^{m+n}\frac{1}{(-C)}\frac{U_{m-1}(-1/C)U_{N-n}(-1/C)}{U_N(-1/C)}, \tag{56}$$

where $U_i(x)$ is a Chebyshev polynomial of the second kind. For $|x| \neq 1$, it is defined as

$$U_n(x) = \frac{r_+^{n+1}-r_-^{n+1}}{r_+-r_-}, \qquad r_\pm = x \pm \sqrt{x^2-1}. \tag{57}$$

In our case $x = -1/C$, and one has

$$U_n(-1/C) = \frac{(-1+\sqrt{1-C^2})^{n+1}-(-1-\sqrt{1-C^2})^{n+1}}{2C^n\sqrt{1-C^2}}. \tag{58}$$

Consider the case of large λ when $C \to 1$. One has $U_n(-1/C) \approx (-1)^n(n+1)$, whence

$$S_{mn}^{-1} = \frac{m(N-n+1)}{N+1}. \tag{59}$$

We are to bear in mind that, because of the difference in $\mathbf{b}_n$ (13), the results for the end beads with $n = 1, N+1$ can differ from that for the inner beads with $2 \leqslant n \leqslant N$. Substituting (59) in (44) gives the correlator for $n > m$ in the limit $C \to 1$,

$$\langle \mathbf{p}_m \mathbf{p}_n \rangle = \frac{MT}{N+1}, \tag{60}$$

which is independent of m and n and valid for inner and end beads. To find $\langle \mathbf{p}_n^2 \rangle$, we set $m = n$ in the general formula (44) with S_{mn}^{-1} (59). The result thus obtained is very different from the above (60),

$$\begin{aligned}\langle \mathbf{p}_n^2 \rangle &= MT\left(3 - \frac{N}{N+1}\right)\\ &= \left(2 + \frac{1}{N+1}\right)MT,\end{aligned} \tag{61}$$

and the energy per bead is $e_\infty = T + \frac{1}{2(N+1)}$, which is very close to but not exactly T. The results (61) are valid both for inner and end beads.

C. Interpolation between the correlators for large and small λ

We have already seen that a number of formulas found in the limit of large λ can quite successfully describe the case of small λ. Here we show how the correlations found for large λ in the previous section can be connected to the correlations found in the Appendix for small λ. To this end we formally explore the above formulas for correlations for small λ and C and indicate the results with an index f (free). In this case, the formulas (56)–(58) give $U_n(-1/C) \simeq (-2/C)^n$ and

$$\left(S_{mn}^{-1}\right)_f = \left(S_{nm}^{-1}\right)_f = \frac{1}{2}\left(\frac{C}{2}\right)^{n-m}, \tag{62}$$

where $n \geqslant m$. This expression is employed in the Appendix for obtaining formula (A28) for the integrals I_{mn} (50), which interpolates between their values for small and large λ. Interpolation formula for the momentum correlator obtains by making use of these I_{mn} in the general formula (44). The result is

$$\begin{aligned}\langle \mathbf{p}_m \mathbf{p}_n \rangle = \langle \mathbf{p}_m \mathbf{p}_n \rangle_0 + 3MT\delta_{mn} - MTC^{n-m}\big(S_{m,n}^{-1} + S_{m-1,n-1}^{-1}\\ - C^{-1}S_{m,n-1}^{-1} - CS_{m-1,n}^{-1}\big),\end{aligned} \tag{63}$$

where the inverse matrix elements are determined by (56)–(58), $C = \coth\lambda - 1/\lambda$, and

$$\langle \mathbf{p}_m \mathbf{p}_n \rangle_0 = -I_{0,mn} - I_{0,m-1,n-1} + I_{0,m-1,n} + I_{0,m,n-1}, \tag{64}$$

where $I_{0,mn}$ are given in (A28) and $I_{0,m,n-1} = I_{0,n-1,m}$ if $m > n-1$. For large λ this formula gives the result (60) and (61), and for small λ the result is determined by I_{mn} found in the Appendix with $(S_{mn}^{-1})_f$ (62). To get the result for a free hinged chain we set $\lambda = C = 0$, which gives

$$\begin{aligned}\langle \mathbf{p}_n \mathbf{p}_{n+1} \rangle &\simeq 0.216MT,\\ \langle \mathbf{p}_n \mathbf{p}_{n+2} \rangle &\simeq 0.091MT,\\ \langle \mathbf{p}_n \mathbf{p}_{n+3} \rangle &\simeq 0.023MT,\\ \langle \mathbf{p}_n \mathbf{p}_{n+4} \rangle &\simeq 0.0057MT,\\ \langle \mathbf{p}_n \mathbf{p}_{n+5} \rangle &\simeq 0.0014MT,\\ \langle \mathbf{p}_n \mathbf{p}_{n+6} \rangle &\simeq 0.00035MT,\\ \langle \mathbf{p}_n^2 \rangle &\simeq 2.57MT,\end{aligned} \tag{65}$$

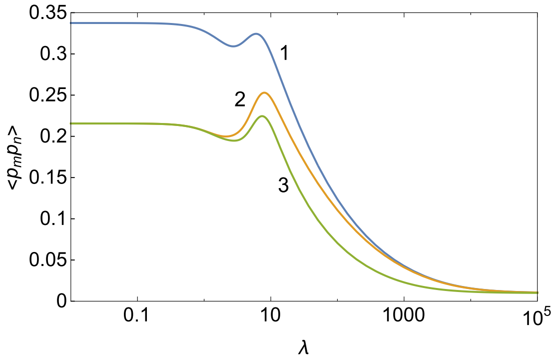

FIG. 4. The momentum correlators (in units TM) $\langle \mathbf{p}_1 \mathbf{p}_2 \rangle$ (curve 1), $\langle \mathbf{p}_2 \mathbf{p}_3 \rangle$ (curve 2), and $\langle \mathbf{p}_{49} \mathbf{p}_{50} \rangle$ (curve 3) vs effective rigidity λ. The figure shows the dependence of the correlators for two neighboring beads on distance from the chain end. $N = 100$.

where $2 \leqslant n$ and the second index is assumed to not exceed N. These results are pertinent to inner beads. We also present some results for the end beads of a free hinged chain:

$$\begin{aligned}\langle \mathbf{p}_1 \mathbf{p}_2 \rangle = \langle \mathbf{p}_N \mathbf{p}_{N+1} \rangle &\simeq 0.34MT,\\ \langle \mathbf{p}_1^2 \rangle = \langle \mathbf{p}_{N+1}^2 \rangle &= 2.5MT.\end{aligned} \tag{66}$$

The orientation correlations can be described with a persistence length for any λ. Formula (54), which is valid for both large and small λ [Eq. (A16)], for $n - m \geqslant 0$ can be presented as

$$\langle \mathbf{t}_m \mathbf{t}_n \rangle = \exp\left[-(n-m)/l_t\right], \tag{67}$$

where $l_t = -1/\ln C$ is the persistence length. As C approaches 1, it slowly diverges and the orientation correlator tends to 1. Inspecting the correlation presented in (65) we notice that for $n - m \geqslant 2$ one can write

$$\langle \mathbf{p}_m \mathbf{p}_n \rangle_{\lambda=0} \simeq 1.46\left(\frac{1}{4}\right)^{n-m} = 1.46\exp\left[-(n-m)/l_0\right], \tag{68}$$

where $l_0 = 0.72l$. This shows that for $\lambda = 0$ the momentum correlations between next and more remote neighbors can be described with a persistence length l_0, but the correlation between neighbors is particular. In contrast to this momentum correlator for a free hinged chain, which rapidly vanishes with distance, the momentum correlator for a very rigid chain, $C \to 1$, tends to the value $MT/(N+1)$ independent of the distance between the beads [Eq. (60)]. This implies that the corresponding correlation length l_p diverges when $C \to 1$. The full analytical expression for the correlations between momenta of two beads is determined by the formulas (55)–(58) (see Figs. 4–6). The numerical results show that $\langle \mathbf{p}_m \mathbf{p}_n \rangle$ depends not only on the distance between the beads $n - m$, but also on their distances m and n from the chain center (or from its end) (see Fig. 4). The mean square momentum $\langle \mathbf{p}_n^2 \rangle$ also depends on the position n of the bead relative to the chain center (see Fig. 6).

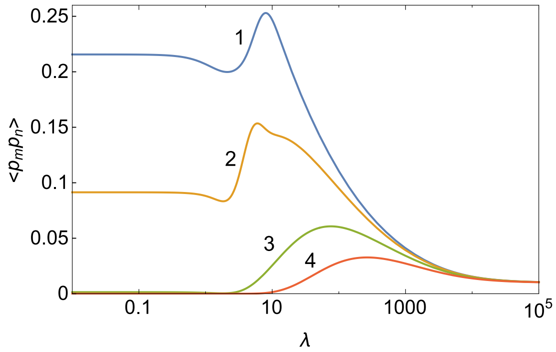

FIG. 5. The momentum correlators (in units TM) $\langle \mathbf{p}_2\mathbf{p}_3\rangle$ (curve 1), $\langle \mathbf{p}_2\mathbf{p}_4\rangle$ (curve 2), $\langle \mathbf{p}_2\mathbf{p}_7\rangle$ (curve 3), and $\langle \mathbf{p}_2\mathbf{p}_{12}\rangle$ (curve 4) vs effective rigidity λ. $N = 100$.

IV. PARTITION FUNCTION AS A THERMODYNAMIC GENERATING FUNCTIONAL

The chain energy E can be obtained as the following sum:

$$E = \sum_{i=1}^{N+1} \frac{\langle \mathbf{p}_i^2\rangle}{2M} - \frac{b}{2}(N-1)\langle\cos\theta\rangle. \tag{69}$$

For $\lambda = 0$ the energy is totally kinetic and, by virtue of (65) and (66), is equal to

$$\begin{aligned} E_0 = E_{\text{kin},0} &= 2\frac{2.5}{2}T + (N-1)\frac{2.57}{2}T \\ &\simeq 1.28(N+1)T; \end{aligned} \tag{70}$$

i.e., the energy per bead is $e_0 = 1.28T$. This differs from the result $e_0' = T$ obtained for a free hinged chain by Edwards and Goodyear [5]. The last result, however, also obtains as the standard derivative $E_{\text{kin}} = -\partial \ln Z_{\text{kin}}/\partial\beta$ from our expression (32) for Z_{kin}, $e' = [1 + \frac{1}{2(N+1)}]T \cong T$ for both large and small λ. For very large λ, this e' coincides with the kinetic energy per bead e_∞ obtained from (61), but for $\lambda = 0$, e_0 is appreciably larger than e'. We stress that, as follows from its derivation, our Z_{kin} for $\lambda = 0$ contains the exact and full dependence on β; hence, the difference between T and $1.28T$ has nothing to do with any approximation. The actual difference lies in the status of the partition function in a system with unresolved constraints.

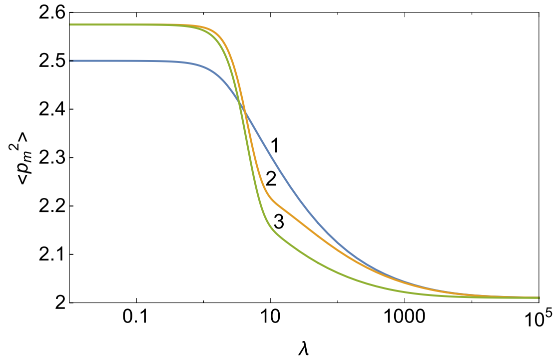

FIG. 6. The mean square momenta (in units TM) $\langle \mathbf{p}_1^2\rangle$ (curve 1), $\langle \mathbf{p}_2^2\rangle$ (curve 2), and $\langle \mathbf{p}_{50}^2\rangle$ (curve 3) vs effective rigidity λ. $N = 100$.

For brevity, here we use the following notations: The product of the δ functions in (7) times $(2\pi\hbar)^{-2N-3}$ is just δ_N, $\int \mathcal{D}\mathbf{t}^N \mathcal{D}\mathbf{p}^{N+1} e^{-\beta H}\delta_N = Z_\xi$, so that $Z = \int \mathcal{D}\xi^N Z_\xi$. Further, the result $e_0 = 1.28T$ is correct as it is obtained directly from the energy definition:

$$E = \langle H\rangle = Z^{-1}\int \mathcal{D}\xi^N(-\partial/\partial\beta)Z_\xi. \tag{71}$$

Hence, the value $e' = -\partial \ln Z/\partial\beta = T$ is not correct. We conclude that the operations of differentiation with respect to β and the integration over the variable ξ, which sets the constraints, cannot be permuted. The authors of [5] first integrated over the variable setting the constraints and then differentiated thus obtained expression which resulted in $e' = T$. It is not difficult to see that the formula with this order, i.e., β differentiation after ξ integration, misses contributions of the integrals I_{mn} with $n \neq m$, which describe correlations between neighbor beads. The difference between $1.28T$ and T is due to such correlations.

For the above reason, the free energy F has to be found from its definition $F = E - TS$, using the definition of E (71) and the definition of entropy. By definition, $S = -\int \mathcal{D}\xi^N \mathcal{D}\mathbf{t}^N \mathcal{D}\mathbf{p}^{N+1} w_{p,t} \ln w_{p,t}'$, where $w_{p,t}$ is the probability of the state $\{p_i,t_i\}$,

$$w_{p,t} = Z^{-1}e^{-\beta H}\delta_N, \tag{72}$$

and $w_{p,t}'$ is $w_{p,t}$ without the singular function δ_N (δ_N in $w_{p,t}$ suffices to fix the constrains). The result is the standard relation $F = -T\ln Z$ and a formula for entropy,

$$S = \ln Z + E/T, \tag{73}$$

where E is given in (71) and Z is given in (30). The standard relation $S = -\partial F/\partial T$ gives this correct result only if the last T derivative is taken under the sign of the ξ integral:

$$S = \ln Z + T\frac{\partial \ln Z}{\partial Z}\int \mathcal{D}\xi^N(\partial/\partial T)Z_\xi \neq -\partial F/\partial T. \tag{74}$$

The conclusion we can draw from our consideration of a polymer chain is quite general. If the constraints are resolved and the system is described by its actual degrees of freedom, then the partition function is the standard function of its parameters. However, in a system with constraints imposed by some integrals over an auxiliary variable ξ, the differentiation with respect to the parameters has to be performed before the ξ integration. Thus, in systems with unresolved constraints the partition function is a generating functional rather than a function on the thermodynamical variables. Of course, there are parameter differentiations with respect to which can be performed directly in Z, where the ξ integration has already been performed. For instance, the total number of particles N in the canonical ensemble does not explicitly appear in the integrand, and the chemical potential can be found as $\partial F/\partial N = -TZ^{-1}\partial Z/\partial N$. In general, however, it is worth bearing in mind that the differentiation before the ξ integration cannot result in a mistake.

V. DISCUSSION AND CONCLUSION

Kinetic energy in the partition functions of polymer chains has been systematically ignored. This can be justified when chains have fixed lengths and the question is only what is the probability of different chains' conformations. If, however, chains are formed in a process of self-assembling in a solution of monomers and their different lengths have different probabilities, then these probabilities themselves must be known; otherwise, the length polydispersity cannot be computed. This is the case of living polymers and versatile aggregation processes. Clearly, the probability of length N is a function of N and the question is how the partition function depends on N. In this case the kinetic energy cannot be ignored as it is the kinetic energy that gives—if not fully dominating, then at the least very essential—contribution to the partition function. Here we incorporated the kinetic energy into the thermodynamics of an inextensible chain and found that its contribution is indeed indispensably considerable. We proposed a nontrivial model of an inextensible chain which is restricted neither to smooth conformations nor to any particular value b/T of the effective rigidity and found its solution. In the very interesting limit of high rigidity we found that the chain backbone gets stretched into a straight line, but the velocities of its segments remain weakly correlated in spite of the fact that their correlation lengths diverge. This means that a rigid chain cannot become a rigid rod because in the rigid rod the velocities of all beads are highly correlated. The amazing result is that the velocity correlations, irrespective of the distance between the beads, tend to the same constant value $\propto T/(N+1)$ as $b/T \to \infty$. Consider this effect energywise.

If the Hamiltonian of a system can be reduced to a sum of n terms quadratic in some coordinates, then this system has n degrees of freedom, consists of n noninteracting harmonic modes, and, by the equipartition theorem [11], its mean energy is $nT/2$. If, however, the Hamiltonian in addition contains some interaction or nonlinear (nonquadratic) terms, the equipartition theorem is not applicable and the total energy can differ from $nT/2$. In this case the energy per degree of freedom is not equal to $T/2$, and one may say that the effective number of degrees of freedom is apparently not n and can be fractional. The number of independent degrees of freedom of the chain is equal to $2N+3$, which is $3(N+1)$ minus the number of the holonomic constrains, N. The total kinetic energy of a rigid chain is equal to $(N+1)T + T/2$, which corresponds exactly to $2N+3$ harmonic modes: $N+1$ ideal two-dimensional oscillators (the oscillation amplitude for rigid chain is very small) plus one harmonic translational degree of motion along the straight backbone. A not-very-rigid chain is both a nonlinear and an interacting system. The bending energy is nonlinear as in a not-rigid chain $\cos\theta$ does not reduce to the harmonic θ^2. A free bead has three degrees of freedom, but in a freely hinged chain, the interaction via links makes beads only partially independent and one degree per bead apparently diminishes to 0.57. As the rigidity increases, these incomplete degrees of freedom undergo further independence loss and, in a rigid chain, all these $(N+1)\times 0.57$ "modes" convert into a single collective mode of motion along the chain's backbone. While in a not-rigid chain all the three bead's modes correlate with those of its neighbors, in a rigid chain the longitudinal modes are correlated much stronger than the transverse modes. The nonmonotonic behavior of the momentum correlations in Figs. 4 and 5 is the result of the interplay between decreasing nonlinearity (decreasing amplitude of the bending angles) and increasing rigidity as λ changes from 0 to ∞. It is in order to note that as our formulas interpolate between small and large values of λ, the small-scale ups and downs of the curves in Figs. 4 and 5 at intermediate $\lambda \sim 10$ might be an artifact of the interpolation. At the same time, the nonmonotonous behavior of curves 3 and 4 in Fig. 5 can be taken with fidelity as they persist over large λ on the order of a few hundred and higher.

In our model, beads interacts via inextensible segments. This interaction is induced by the constraints, which makes it very different from the standard interaction in the form of potential energy. Indeed, N holonomic constraints eliminate N degrees of freedom and result in the partition function where the momentum and coordinate integrals are not factorized. If, however, the rigid link is replaced by a potential which smoothly increases with the link extension, then one has the (in general) nonlinear bead-spring model: The number of degrees of freedom is not reduced and the momentum and coordinate integrals are factorized however steeply the energy penalty for the link extension rises. Similarly to our result that a rigid chain cannot become a rigid rode, the two models cannot go over into each other for any smooth potential. The fundamental reason is that the number of actual degrees of freedom, which is $2N+3$ in our model and $3(N+1)$ in the bead-spring model, is not the model's output but its input which cannot change. Thus, the two models describe different physical systems. A system of our interest with inextensible links can be described by the following example. The rodlike links between beads represent certain quantum bonds. The spectrum of a quantum rod is quantized. If the first excitation of its longitudinal mode has the energy which is much larger than the thermal energy T, then the rod can be considered inextensible. At the same time, the moment of inertia of the rod can be large enough so that the spectrum of its rotations about the joints is effectively continuous (the quant of rotation energy is inverse proportional to the moment of inertia). A chain consisting of such rods can be described by our model.

The appearance of the collective variable N in the partition function points to certain collective mode in the motion of a rigid chain. The importance of such terms N^q in partition functions of linear aggregates has been recently predicted by one of us in Refs. [7,8]: It was shown that the parameter q in these terms fully determines the polydispersity dependence on the monomer concentration c via the terms of the form $c^{q/(q+1)}$, $c^{(q+1)/(q+2)}$, $c^{-1/(q+2)}$. However, the dependence N^q in [7,8] was only assumed to model the effect of collective translation-rotation degrees of motion of linear aggregates. In this paper such dependence $N^{-1/2}$ was found for a rigid chain, which justifies the model proposed in [7,8]. An interesting related question which has not been addressed so far is incorporation of the kinetic energy in the thermodynamics of an actually continuous wormlike object, which consists not of independent links, but of an elastic material that cannot be presented as a collection of more elementary units. If very rigid, that would be a hard rod indeed. This problem arises, e.g., in the physics of chromonic liquid crystals [4], where aggregates are stacks of planklike dye molecules. The neighboring dye molecules are strongly connected via overlapping of their π orbitals and cannot move independently of one another so that such linear chains are flexible but very rigid. Their length depends on the monomer concentration c, and if c is sufficiently large, interaction of linear aggregates in an isotropic solvent result in their orientation along a common direction and transition of the system to a lyotropic chromonic nematic phase [4]. A much stronger effect has been observed when an isotropic solvent was replaced with anisotropic one, a thermotropic nematic liquid crystal [13,14]. In this case aggregates are much longer so that they length segregate: The longest chains separate into dense elongated regions seen under a microscope [14]. Clearly, all these effects essentially depend on the chains' polydispersity, to which the kinetic energy is expected to contribute significantly. The problem is more complicated than the one of a single chain considered here as the self-assembling in a nematic medium is influenced by chains' interaction with one another via the nematic elasticity. Are such aggregates rigid chains considered here or continuous wormlike objects? To answer, we need to find the N dependence of the worm's free energy. We shall address this problem in our future study.

APPENDIX: PARTITION FUNCTION AND CORRELATIONS IN THE CASE OF SMALL λ

1. Partition function for small λ

Here we find the partition function of the chain up to small terms $\sim \lambda^2$ and show that its analytical form is practically the same as given by the formulas (30)–(33). To find the results for small λ we assume that the number of beads $N+1$ is large and neglect the terms $O(1/N)$. For $\lambda \to 0$, the expansion R (24) is useless as the coefficients in the square brackets diverge for $n > 4$. We now expand the product in the integrand of Z' (19). For brevity, we put $\xi_i \xi_{i+1} = x_i$ so that $a_i = \lambda + x_i$. Then, retaining only terms linear and quadratic in λ, one has

$$\frac{\sinh(\lambda + x_i)}{\lambda + x_i} = \frac{\sinh\lambda}{\lambda} + Y_i, \tag{A1}$$

where

$$Y_i = \frac{x_i^2 + 2\lambda x_i}{3!} + \frac{x_i^4 + 4\lambda x_i^3 + 6\lambda^2 x_i^2}{5!} + \frac{x_i^6 + 6\lambda x_i^5 + 15\lambda^2 x_i^4}{7!} + \cdots . \tag{A2}$$

The partition function Z' (19) now has the form

$$Z' = \int \mathcal{D}\xi^N \exp\left(-\frac{1}{2}\sum_{k=1}^{N} 2\xi_k^2\right) \times \Pi_0, \tag{A3}$$

where

$$\Pi_0 = \prod_{i=1}^{N-1}\left(\frac{\sinh\lambda}{\lambda} + Y_i\right). \tag{A4}$$

The matrix $S_{0,kk'} = 2\delta_{kk'}$ of the quadratic form in (A3) is diagonal so that the inverse matrix is also diagonal:

$$S^{-1}_{0,kk'} = \tfrac{1}{2}\delta_{kk'}. \tag{A5}$$

Consider the product (A4):

$$\Pi_0 = \left(\frac{\sinh\lambda}{\lambda}\right)^{N-1} + \left(\frac{\sinh\lambda}{\lambda}\right)^{N-2}\sum_{i=1} Y_i + \left(\frac{\sinh\lambda}{\lambda}\right)^{N-3}\sum_{i<j} Y_i Y_j + \cdots . \tag{A6}$$

The terms linear in λ do not contribute to Z': These terms in Π have the form $x_i, x_i^3, \ldots, x_i x_j, x_i x_j^3, \ldots, x_i^{2n-1} x_j^{2k+1}$; they are proportional to ξ_i^{2n-1} and vanish after the ξ_i integration from $-\infty$ to ∞. Further, Z' without these terms is the sum of integrals of the well-known type [15]

$$\int \mathcal{D}\xi^N \xi_{i_1}\cdots\xi_{i_{2n}} \exp\left(-\frac{1}{2}\sum_{k=1}^{N} S_{0,kk}\xi_k^2\right) = \sqrt{\frac{(2\pi)^N}{|\det S_0|}} \sum_{\substack{\text{all pairings} \\ \text{of } \{i_i, i_2, \ldots, i_{2n}\}}} S^{-1}_{0,i_{p_1} i_{p_2}} \cdots S^{-1}_{0,i_{p_{2n-1}} i_{p_{2n}}}, \tag{A7}$$

where $\det S_0 = 2^N$. Let us apply this formula to Y_i. Since the matrix S_0 is diagonal, only pairings between the same variables ξ_i are nonzero. The total number of terms with different pairings in $x_i^{2n} = \xi_i^{2n}\xi_{i+1}^{2n}$ is equal to the number of pairings between $2n$ variables ξ_i times the number of pairings between $2n$ variables ξ_{i+1}, which gives $[2n(2n-1)/2]^2$. Each term is a product of $2n$ pairings, each one being $1/2$. Then one gets

$$\begin{aligned}\overline{Y} &= \pi^{-N/2}\int \mathcal{D}\xi^N Y_i \exp\left(-\sum_{k=1}^{N}\xi_k^2\right) \\ &= \sum_{n=1} \frac{n^2(2n-1)^2}{2^{2n}(2n+1)!} \\ &\quad + \lambda^2 \sum_{n=1} \frac{(2n)!}{(2n-2)!2!}\,\frac{(2n-2)^2(2n-3)^2}{2^2(2n+1)!2^{2n-2}} \\ &\cong 0.06 + 0.02\lambda^2.\end{aligned} \tag{A8}$$

The above pairing counting and the result (A8) will be employed in our further calculations.

Now consider the ξ integral of the product $Y_i Y_j$, which consists of the terms $x_i^{2n} x_j^{2m}$. For $j > i+1$, there are no pairings between variables from x_i^{2n} and x_j^{2m}, and the integral factorizes like that:

$$\begin{aligned}&\int \mathcal{D}\xi^N x_i^{2n} x_j^{2m} \exp\left(-\sum_{k=1}^{N}\xi_k^2\right) \\ &= \pi^{N/2}[2n(2n-1)/2][2m(2m-1)/2]\frac{1}{2^{m+n}} \\ &= \pi^{N/2}\int \mathcal{D}\xi^N \frac{x_i^{2n}}{\pi^{N/2}} \exp\left(-\sum_{k=1}^{N}\xi_k^2\right) \\ &\quad \times \int \mathcal{D}\xi^N \frac{x_j^{2m}}{\pi^{N/2}} \exp\left(-\sum_{k=1}^{N}\xi_k^2\right).\end{aligned} \tag{A9}$$

Similarly, if all indices $i, j, \ldots, k, l$ in the product $x_i^{2n_i} x_j^{2n_j} \cdots x_k^{2n_k} x_l^{2n_l}$ differ from one another by more than

1, then the integral over ξ^N of this product is equal to the product of the ξ integrals of $x_i^{2n_i}/\pi^{N/2}, x_j^{2n_j}/\pi^{N/2}, \ldots$, and $x_l^{2n_l}/\pi^{N/2}$. It follows then that the same is true about the product $Y_i Y_j \cdots Y_k Y_l$. It now remains to observe that (a) the overwhelming contribution to the partition function comes from the terms whose order in Y is small compared to N; (b) for large N, in products $Y_i Y_j \cdots Y_k$ of such orders, the number of terms with the neighboring indices (i.e., differing by ± 1) is negligible as compared to those with indices differing by more than one. For instance, in the sum $\sum_{i<j} x_i x_j$ there are $(N-2)$ terms of the form $x_i x_{i+1}$ and $(N-1)(N-2)/2-(N-1)$ terms without neighboring indices. Thus, the terms without neighboring indices dominate in the product (A6), and we can neglect pairings between variables ξ belonging to different Y_i. It is then not difficult to see that the result of integration in (A3) reduces to $\pi^{N/2}$ times Π in which each Y_i is replaced with $\overline{Y}$. We finally obtain

$$\begin{aligned} Z' &\simeq \pi^{N/2}\left[\left(\frac{\sinh\lambda}{\lambda}\right)^{N-1} + \left(\frac{\sinh\lambda}{\lambda}\right)^{N-2}(N-1)\overline{Y} \right. \\ &\quad \left. + \left(\frac{\sinh\lambda}{\lambda}\right)^{N-2}\frac{(N-1)(N-2)}{2}\overline{Y}^2 + \cdots\right] \\ &\simeq \left(\frac{2\pi}{2}\right)^{N/2}\left(\frac{\sinh\lambda}{\lambda} + 0.061 + 0.02\lambda^2\right)^{N-1}. \end{aligned} \tag{A10}$$

2. Momentum and orientation correlators: Integrals I_{mn} for small λ

For small λ the Gaussian approximation fails and we expand each factor in a power series of x_i. Consider first the orientational correlator (51),

$$\langle \mathbf{t}_m \mathbf{t}_n \rangle = \frac{(4\pi)^N}{Z}\int \mathcal{D}\xi^N \exp\left(-\sum_{k=1}^{N}\xi_k^2\right) \times \Upsilon_{n-m}\Pi_{n-m}, \tag{A11}$$

where $n > m$ and

$$\begin{aligned} \Upsilon_{m-n} &= \prod_{i=m,m+1,\ldots,n-1}\left(\frac{\cosh\lambda}{\lambda} - \frac{\sinh\lambda}{\lambda^2} + \widetilde{Y}_i\right), \\ \Pi_{n-m} &= \prod_{i\neq m,m+1,\ldots,n-1}\left(\frac{\sinh\lambda}{\lambda} + Y_i\right). \end{aligned} \tag{A12}$$

Here Y_i is given in (A2) and

$$\begin{aligned} \widetilde{Y}_i &= x_i\left(\frac{1}{2!} - \frac{1}{3!}\right) + \left(x_i^3 + 3\lambda^2 x_i + 3\lambda x_i^2\right)\left(\frac{1}{4!} - \frac{1}{5!}\right) \\ &\quad + \left(x_i^5 + 10\lambda^2 x_i^3 + 10\lambda^3 x_i^2 + 5x_i\lambda^4 + 5x_i^4\lambda\right)\left(\frac{1}{6!} - \frac{1}{7!}\right) \\ &\quad + \cdots . \end{aligned} \tag{A13}$$

For $m = n$, $\Pi_{n-m} = \Pi_0$ [Eq. (A4)] and $\Upsilon_{m-n} = 1$. By similarity with Eq. (A8), we introduce the quantity

$$\overline{\widetilde{Y}} = \int \mathcal{D}\xi \frac{\widetilde{Y}_i}{\pi^{N/2}}\exp\left(-\frac{1}{2}\sum_{k=1}^{N} S_{0,kk}\xi_k^2\right), \tag{A14}$$

which does not depend on the index i. The odd powers of x_i do not contribute to this integral. Retaining only terms linear in λ and counting pairings as in the case of the partition function, one finds

$$\begin{aligned} \overline{\widetilde{Y}} &= \lambda\sum_{n=1}\frac{n^2(2n-1)^2(2n+1)!}{2^{2n}(2n)!}\left[\frac{1}{(2n)!} - \frac{1}{(2n+1)!}\right] \\ &\cong 0.0039\lambda. \end{aligned} \tag{A15}$$

As in the above case of the partition function, neglecting terms of the order $1/N$, we have

$$\begin{aligned} \langle \mathbf{t}_m \mathbf{t}_n \rangle &= \frac{(4\pi)^N}{Z}\left(\frac{\cosh\lambda}{\lambda} - \frac{\sinh\lambda}{\lambda^2} + \overline{\widetilde{Y}}\right)^{n-m} \\ &\quad \times \left(\frac{\sinh\lambda}{\lambda} + \overline{Y}\right)^{N-(n-m)} \\ &= \left(\frac{\cosh\lambda/\lambda - \sinh\lambda/\lambda^2 + 0.0039\lambda}{\sinh\lambda/\lambda + 0.061 + 0.02\lambda^2}\right)^{n-m} \\ &\simeq C^{n-m}, \end{aligned} \tag{A16}$$

which coincides with the correspondent formula (54) for large λ. In particular, $\langle\cos\theta\rangle \simeq C$ both for small and for large λ.

To find the momentum correlations, one needs to find I_{mn} (50), which implies solving the integral

$$\begin{aligned} I_{mn} &= \frac{(2\pi)^N 2^N}{Z}\frac{M}{\beta}\int \mathcal{D}\xi^N \exp\left(-\frac{1}{2}\sum_{k=1}^{N} S_{0,kk}\xi_k^2\right) \\ &\quad \times J_{n-m}\Pi_{n-m}, \end{aligned} \tag{A17}$$

where $J_{m-n} = \xi_m \xi_n \Upsilon_{m-n}$. For $m = n$ the result is straightforward; i.e.,

$$I_{nn} = \frac{1}{2}\frac{M}{\beta}. \tag{A18}$$

Now assume that $n > m$. As in the above calculation of the partition function, within accuracy up to terms $O(1/N)$, one has

$$\begin{aligned} I_{n-m} &\propto \int \mathcal{D}\xi^N \exp\left(-\frac{1}{2}\sum_{k=1}^{N} S_{0,kk}\xi_k^2\right) \times J_{n-m}\Pi_{n-m} \\ &= \pi^{N/2}\overline{J}_{n-m}\left(\frac{\sinh\lambda}{\lambda} + \overline{Y}\right)^{N-1-(n-m)}, \end{aligned} \tag{A19}$$

where $\overline{Y}$ is given in (A8) and

$$\overline{J}_{n-m} = \int \mathcal{D}\xi \frac{J_{n-m}}{\pi^{N/2}}\exp\left(-\frac{1}{2}\sum_{k=1}^{N} S_{0,kk}\xi_k^2\right). \tag{A20}$$

We consider the cases with $n - m = 1$, 2, and 3 individually. Notice that any odd power of ξ on the ξ integration gives zero; hence, we retain only terms with even powers of ξ_i. For

$n - m = 1$ one has

$$\begin{aligned} J_1 &= \xi_n \xi_{n+1} \left(\frac{\cosh\lambda}{\lambda} - \frac{\sinh\lambda}{\lambda^2} + \widetilde{Y}_n \right) \\ &\to \xi_n^2 \xi_{n+1}^2 \left(\frac{1}{2!} - \frac{1}{3!} \right) + \left(\xi_n^4 \xi_{n+1}^4 + 3\xi_n^2 \xi_{n+1}^2 \lambda^2 \right) \left(\frac{1}{4!} - \frac{1}{5!} \right) \\ &\quad + \left(\xi_n^6 \xi_{n+1}^6 + 10\xi_n^4 \xi_{n+1}^4 \lambda^2 \right) \left(\frac{1}{6!} - \frac{1}{7!} \right) + \cdots . \end{aligned} \tag{A21}$$

Counting pairings as in the above case of partition function, one finds

$$\begin{aligned} \overline{J}_1 &= \sum_{n=1} \frac{n^2(2n-1)^2}{2^{2n}} \left[\frac{1}{(2n)!} - \frac{1}{(2n+1)!} \right] \\ &\quad + \lambda^2 \sum_{n=1} \frac{(2n+1)!}{(2n-1)!2!} \frac{n^2(2n-1)^2}{2^{2n}} \\ &\quad \times \left[\frac{1}{(2n+2)!} - \frac{1}{(2n+3)!} \right] \\ &\cong 0.163 + 0.053\lambda^2. \end{aligned} \tag{A22}$$

Substituting this formula in $I_{n,n+1}$ (50) results in

$$I_{n,n+1} = \frac{M}{\beta} \frac{0.163 + 0.053\lambda^2}{\sinh\lambda/\lambda}. \tag{A23}$$

Now we address the case $n - m = 2$ when J_2 has the form

$$\begin{aligned} J_2 = \xi_n \xi_{n+2} &\left(\frac{\cosh\lambda}{\lambda} - \frac{\sinh\lambda}{\lambda^2} + \widetilde{Y}_n \right) \\ \times &\left(\frac{\cosh\lambda}{\lambda} - \frac{\sinh\lambda}{\lambda^2} + \widetilde{Y}_{n+1} \right). \end{aligned} \tag{A24}$$

Finding $\overline{J}_2$ is now an elaborated problem as it is difficult to present the result in the form of series as in (A22). Instead, one collects all the even order terms which give a substantial contribution and ceases the summation on realizing that the neglected terms are negligible. Note that only terms of the form $\xi_n x_n^{2k+1} x_{n+1}^{2k'+1} \xi_{n+2}$ give nonzero contributions to $\overline{J}_2$. The result is $\overline{J}_2 \simeq 0.045 + 0.25\lambda^2 + 0.0062\lambda^4$, and one obtains

$$I_{n,n+2} = \frac{M}{\beta} \frac{0.045 + 0.025\lambda^2 + 0.0062\lambda^4}{(\sinh\lambda/\lambda)^2}. \tag{A25}$$

We also found the constant term in the case $n - m = 3$. The result is

$$I_{n,n+3} = \frac{M}{\beta} \frac{0.001 + \cdots}{(\sinh\lambda/\lambda)^3}. \tag{A26}$$

3. Momentum correlations: Interpolation from large to small λ

We know that the orientational correlators for large and small λ practically coincide; see Eqs. (54) and (A16). This prompts that the momentum correlations for large and small λ can also be described, if not by the same formula, then by certain interpolating expression. We know that the correlator $\langle \mathbf{p}_m \mathbf{p}_n \rangle$ for any λ is determined by the integrals I_{mn} via the general formula (44), that for large λ these quantities are given by the product $C^{m-n} S_{mn}^{-1}$, Sec. III B, and for small λ the lowest order I_{mn} are given by Eqs. (A24)–(A26) and (A18). The idea is to express these small-λ expressions in terms of the large-λ term $C^{m-n} S_{mn}^{-1}$ but with $(S_{mn}^{-1})_f = (1/2)(C/2)^{n-m}$ (62) formally obtained for small λ. To this end we compare the small λ asymptotics of the pertinent quantities with the expressions (A24)–(A26) and (A18). For $\lambda \ll 1$, one has

$$\begin{aligned} C &\simeq \lambda/3, \\ \frac{\cosh\lambda}{\lambda} - \frac{\sinh\lambda}{\lambda^2} &\simeq \lambda/3, \\ C\left(S_{n,n+1}^{-1}\right)_f &\simeq \lambda^2/36 \simeq 0.028\lambda^2, \\ C^2\left(S_{n,n+2}^{-1}\right)_f &= 0.0015\lambda^4. \end{aligned} \tag{A27}$$

In the next step, one realizes that the constants in (A24)–(A26) obey the following relation: $I_{n,n+2}(0)/I_{n,n+1}(0) \simeq I_{n,n+3}(0)/I_{n,n+2}(0) \simeq 4$. Then, indicating the case of small λ by subscript 0, one can write

$$\begin{aligned} I_{0,nn} &= 0, \\ I_{0,n,n+1} &= \frac{M}{\beta} \left[\frac{0.65}{4\sinh\lambda/\lambda} + \frac{0.025\lambda^2}{\sinh\lambda/\lambda} + C\left(S_{n,n+1}^{-1}\right)_f \right], \\ I_{0,n,n+2} &= \frac{M}{\beta} \left[\frac{0.65}{(4\sinh\lambda/\lambda)^2} + \frac{0.025\lambda^2 + 0.0045\lambda^4}{(\sinh\lambda/\lambda)^2} \right. \\ &\quad \left. + C^2\left(S_{n,n+2}^{-1}\right)_f \right], \\ I_{0,n,n+3} &= \frac{M}{\beta} \frac{0.65}{(4\sinh\lambda/\lambda)^3} + \cdots . \end{aligned} \tag{A28}$$

The integral $I_{0,nn}$ is set zero as its value $1/2(M/\beta)$ is attributed to the term $(S_{n,n}^{-1})_f$, which is already present in the formula (52) for I_{nn}. Here we replaced 0.163 in (A23) with 0.65/4 and so on. Since $(S_{n,n+1}^{-1})_f$ and $S_{n,n+1}^{-1}$ for large λ are obtained from the same formulas (56)–(58), in (A28) we can replace $(S_{n,n+2}^{-1})_f$ with the general $S_{n,n+2}^{-1}$. If $m < n - 1$, then $I_{0,m,n-1}$ is replaced by $I_{0,n-1,m}$; see Eq. (56). These $I_{0,mn}$ are converted to the momentum correlators in Sec. III C.

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