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On the Generalized Borel Transform and Its Application to the Statistical Mechanics of Macromolecules

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On the generalized Borel transform and its application to the statistical mechanics of macromolecules

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We present a new integral transform called the generalized Borel transform (GBT) and show how to use it to compute distribution functions used to describe the statistical mechanics of macromolecules. For this purpose, we choose the random flight model (RFM) of macromolecules and show that the application of the GBT to this model leads to the exact expression of the polymer propagator (two-point correlation function) from which all the statistical properties of the model can be obtained. We also discuss the mathematical simplicity of the GBT and its applicability to macromolecules with other topologies. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1618361]

I. INTRODUCTION

Consider a group of n small molecules with identical molecular structures. Furthermore, let us assume that these small molecules are connected in a sequential manner such that each of them has only two nearest neighbors with whom it forms chemical bonds. The small molecules at the ends of the chain form only one bond (they have only one neighbor). This macromolecule is called a polymer and each small molecule in the polymer is called a monomer. If the chain ends are free (they do not form a chemical bond), then the polymer is said to have a linear topology (linear polymer). Figure 1 shows this topology. If the ends were to form a chemical bond, then the polymer is said to be a ring (cyclic) polymer as showed in Fig. 1. Another way of connecting the monomers is to grow m linear polymers from a point where all the polymers form chemical bonds to each other. This is a well known topology called the star topology and defines an m-arm star polymer. Combinations of these three topologies or new topologies like dendritic topologies define more complex macromolecules.

Let us now consider the case when there are different kinds of monomers. In other words, let us assume that there are many groups of monomers such that the molecular structures of the groups are different. Then, we can connect these different monomers to form polymers which, in this case, are called copolymers. Again, linear, ring and star copolymers are possible. But, due to the different molecular structures of the groups, the distribution of the different monomers along the polymer will influence its physical properties. Thus, the probability distribution of finding a monomer with a specific molecular structure along the polymer must be known *a priori* so that the physical properties can be computed.

In order to calculate the statistical properties of the aforementioned systems, we have to use coarse-grained models. The procedure for this is well known:[1] we have to group m consecutive monomers into a statistical (Kuhn) segment of length l ($=$Kuhn length).[2] Thus, we replace the real polymer with n monomers by an equivalent polymer with n/m Kuhn segments such that the long wavelength properties are not altered. This equivalent model is the random flight model (RFM) of polymers.[1,3,4] Figure 2 shows the RFM.

The statistical properties of the RFM are computed from distribution functions like the single

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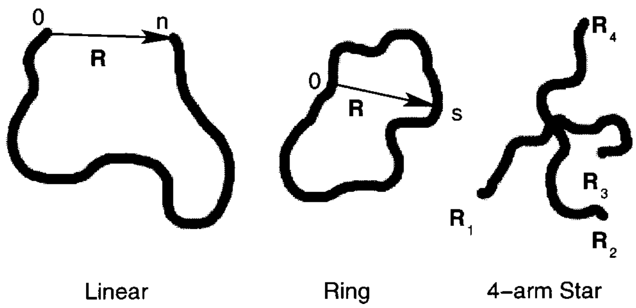

FIG. 1. Linear, ring and four-arm star topologies for flexible polymers. **R** indicates the end-to-end vector for the linear topology and the relative position of two segments in the case of a ring polymer. $\mathbf{R}_j$ indicates the position of the end of the jth arm in the star topology.

chain static structure factor (which is the density-density autocorrelation function in reciprocal space), the probability distribution of the end-to-end distance (polymer propagator) in a linear polymer or its Fourier transform called the characteristic function.[1,3–5] In particular, the polymer propagator is a very useful quantity because all the statistical properties of the model can be calculated from it. For example, the partition function of the model is the integral of the polymer propagator. Therefore, in this article we focus on the exact calculation of the polymer propagator for flexible polymers/copolymers with different topologies. For this purpose, we describe a new integral transform called the generalized Borel transform[6–8] (GBT) and apply it to the computation of the polymer propagator.

The polymer propagator of the RFM of linear polymers is defined as follows:

$$P(\mathbf{R},n)=\int d\{\mathbf{R}_k\}\prod_{j=1}^{n}\tau(\mathbf{R}_j)\,\delta\left(\sum_{j=1}^{n}\mathbf{R}_j-\mathbf{R}\right), \tag{1}$$

where **R** is the end-to-end vector and $\mathbf{R}_j$ is the bond vector between the $(j-1)$th and jth beads. The Dirac delta imposes the condition that the sum of the bond vectors has to be equal to the end-to-end vector. $\tau(\mathbf{R}_j)$ is given by the formula

$$\tau(\mathbf{R}_j)=\frac{\delta(|\mathbf{R}_j|-l)}{4\pi l^2}, \tag{2}$$

and fixes the length of each bond vector to the Kuhn length, l.

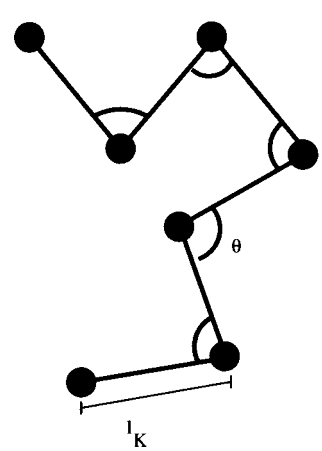

FIG. 2. The random flight model of polymer chains. l is the Kuhn length and θ is the bond angle.

Small changes to Eq. (1) can be used to describe other topologies. For example, ring polymers can be described by Eq. (1) if the constraint $\delta(\Sigma_{j=1}^{n}\mathbf{R}_j)$ is included in the integrand and the constraint $\delta(\Sigma_{j=1}^{n}\mathbf{R}_j-\mathbf{R})$ is replaced by $\delta(\Sigma_{j=s}^{s'}\mathbf{R}_j-\mathbf{R})$ where now $\mathbf{R}$ is the vector going from the s to the s' segments. Similarly, other constraints can be included in Eq. (1) to describe other topologies.

A generalization of Eq. (1) valid for copolymers under external fields has the following mathematical expression:

$$P(\mathbf{R},n,\{p_j^{\alpha}\})=\int d\{\mathbf{R}_k\}\prod_{j=1}^{n}\left(\sum_{\alpha=1}^{x}(p_j^{\alpha}\ \tau_j^{\alpha}(\mathbf{R}_j))\right)\delta\left(\sum_{j=1}^{n}\mathbf{R}_j-\mathbf{R}\right)\exp(-\omega(\{\mathbf{R}_j\})), \tag{3}$$

where x is the total number of different groups of segments forming the copolymer, p_j^{α} is the probability of finding the jth segment in the αth group of segments and $\omega(\{\mathbf{R}_j\})$ has the mathematical form

$$\omega(\{\mathbf{R}_j\})=\sum_{j=1}^{n}\ \eta(\mathbf{R}_j), \tag{4}$$

where $\eta(\mathbf{R})$ can be any function. In particular, the effects of external vectorial $[\eta(\mathbf{R})=-\mathbf{F}\cdot\mathbf{R}]$ and quadrupolar $[\eta(\mathbf{R})=Q_{ij}R_iR_j]$ fields can be studied.

Using the exponential representation of Dirac's delta,[9] Eq. (3) can be written as follows:

$$P(\mathbf{R},n,\{p_j^{\alpha}\})=\int\frac{d^3k}{(2\pi)^3}\exp(-i\mathbf{R}\cdot\mathbf{k})K(\mathbf{k},n,x,l,\{p_j^{\alpha}\}), \tag{5}$$

where $K(\mathbf{k},n,x,l,\{p_j^{\alpha}\})$ is the characteristic function. In the particular case of an isotropic system (i.e., no external fields), Eq. (5) becomes a Fourier sine transform which, for all the models described above, is exactly doable using the GBT technique.

For the purpose of simplicity, in this article we show how to apply the GBT to the case of a linear polymer with only one kind of segment. Afterward, the results obtained for this case are generalized to the case of ring and m-arm star polymers.

This article is organized as follows. In Sec. II we show how to calculate Fourier sine transforms using the generalized Borel transform and present a brief summary of the mathematical aspects of this technique. In Sec. III we apply the GBT to solve exactly a particular Fourier sine transform which is relevant to the computation of the polymer propagator of the RFM. This result is used to obtain the exact polymer propagator of the RFM. Finally, in Sec. IV we present the conclusions of our work.

II. THE GENERALIZED BOREL TRANSFORM

In the previous section we have shown that the Fourier sine transform plays a very important role in the evaluation of the statistical properties of models for single macromolecules. Therefore, let us start the description of the GBT by writing the general expression of a Fourier sine transform of a function $H(k,a)$,

$$Q(R,a)=\int_0^{\infty}\sin(Rk)H(k,a)dk. \tag{6}$$

Furthermore, let us assume that the Laplace transform of the same function, $S(g,a)$, exists. Then, we can write

$$S(g,a)=\int_0^{\infty}H(x,a)\exp(-gx)dx,\quad g>0. \tag{7}$$

Then, we observe that we can obtain the Fourier sine transform, $Q(R,a)$, from the Laplace transform, $S(g,a)$, as the analytic continuation of $S(g,a)$ to the complex plane as follows:

$$Q(R,a)=\mathrm{Im}\{S(g=-iR,a)\}. \tag{8}$$

Consequently, we will focus on the evaluation of Laplace transforms. For this purpose, we will employ the GBT technique described hereafter.

The main goal of the GBT is to obtain analytical solutions of parametric integrals of the Mellin/Laplace type[6–8] for all the range of values of the parameters. Therefore, this technique is very useful to study nonperturbative regimes. The basic idea of the method consists of introducing two auxiliary functions, $S(g,a,n)$ and $B_\lambda(s,a,n)$ (the generalized Borel transform). These functions depend on auxiliary parameters called n and λ. These parameters have no physical meaning and are introduced for the sole purpose of helping in the computation of an explicit mathematical expression for $S(g,a)$ valid for all values of the true parameters g and a.

Let us start with the mathematical definition of $S(g,a,n)$, which is the following:

$$S(g,a,n)=\int_0^\infty x^n H(x,a)\exp(-gx)dx, \quad g>0. \tag{9}$$

We have explicitly extracted a factor x^n from the function to be transformed. This integral is related to the Laplace transform, Eq. (7), by the following relationship,

$$S(g,a,n)=(-)^n \frac{\partial^n}{\partial g^n} S(g,a), \tag{10}$$

which can be inverted to give

$$S(g,a)=(-)^n \underbrace{\int dg \cdots \int dg}_{n} S(g,a,n)+\sum_{p=0}^{n-1} c_p(a,n) g^p. \tag{11}$$

The finite sum comes from the indefinite integrations. Note that all the coefficients vanish whenever the Laplace transform, Eq. (7), fulfills the following asymptotic condition:

$$\lim_{g\to\infty} S(g,a)=0. \tag{12}$$

In addition, the expression given by Eq. (11) is valid for any value of the parameter n, in particular for $n \gg 1$ where the GBT provides an approximate analytical expression for $S(g,a,n)$ as we describe below.

Let us define the generalized Borel transform of $S(g,a,n)$ as follows:

$$B_\lambda(s,a,n)\equiv-\int_0^\infty \exp[s/\eta(g)]\left[\frac{1}{\lambda\,\eta(g)}+1\right]^{-\lambda s}\frac{S(g,a,n)}{[\eta(g)]^2}\frac{\partial \eta(g)}{\partial g}dg, \quad \mathrm{Re}(s)<0 \tag{13}$$

where λ is any real, positive, and nonzero number, and η is defined as follows: $1/\eta \equiv \lambda(\exp(g/\lambda)-1)$. Then, it can be proved that $B_\lambda(s,a,n)$ is an analytic function for real values of s less than zero. Moreover, the analytic continuation to the other half of the complex plane generates an analytic function with a cut on the positive real axis.

In order to invert the transform defined by Eq. (13), we note that the change of variables $u(g)=1/\eta-\lambda \ln[1+1/\lambda\,\eta]$ transforms the integral, Eq. (13), into a Laplace transform,

$$B_\lambda(s,a,n)\equiv\int_0^\infty \exp[su]L_\lambda(S,a,n,u)du, \quad \mathrm{Re}(s)<0, \tag{14}$$

where $L_\lambda(S,a,n,u)$ depends on $S(g,a,n)$. Consequently, the inverse Laplace transform of Eq. (14) provides a procedure for the evaluation of $S(g,a,n)$ by integrating $B_\lambda(s,a,n)$ on the imaginary axis or over the discontinuity of $B_\lambda(s,a,n)$ on the cut. After a change of variables we can write $S(g,a,n)$ as follows:

$$S(g,a,n)=2\lambda^2(1-\exp(-g/\lambda))\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp[G(w,t,g,\lambda,a,n)]dw\,dt. \tag{15}$$

$G(w,t,g,\lambda,a,n)$ is given by the following expression:[6]

$$G(w,t,g,\lambda,a,n)=-s(t)u(g)+t-\ln\{\Gamma[\lambda(s(t)+x(w))]\} \\ +\{\lambda[s(t)+x(w)]-1\}\ln(\lambda s(t))-\lambda s(t)+w+\ln[x(w)^n H(x(w))], \tag{16}$$

where $s(t)=\lambda\exp(t)$ and $x(w)=\exp(w)$.

Note that Eq. (15) is valid for any nonzero, real and positive value of the parameter λ. However, the resulting expression for $S(g,a,n)$ does not depend on λ explicitly. Thus, each value of the parameter λ defines a particular Borel transform. Consequently, we can choose the value of this parameter in such a way that it allows us to solve Eq. (15).

The dominant contribution to the double integral is obtained using steepest descent[10,11] in the variables t and w. For this purpose, we first compute the expressions of the saddle point $t_o(g,a,n)$ and $w_o(g,a,n)$ in the limit $\lambda \gg 1$. The results are the following:

$$t_o(g,a,n)=\ln\left[\frac{x_o^2(g,a,n)}{f(x_o(g,a,n),a,n)}\right], \quad w_o(g,a,n)=\ln[x_o(g,a,n)], \tag{17}$$

where $x_o(g,a,n)$ is the real and positive solution of the implicit equation coming from the extremes of the function $G(w,t,g,\lambda,a,n)$ in the asymptotic limit in λ. Explicitly, the equation is

$$x_o^2 g^2=f(x_o,a,n)[f(x_o,a,n)+1], \tag{18}$$

where

$$f(x_o,a,n)\equiv 1+n+x_o\frac{d\ln[H(x_o,a)]}{dx_o}. \tag{19}$$

Afterward, we check the positivity condition[12] [the Hessian of $G(w,t,g,\lambda,a,n)$ at the saddle point must be positive]. Let us call the Hessian $D(x_o,a,n)$. Its mathematical expression is

$$D(x_o,a,n)\equiv -x_o\frac{df(x_o,a,n)}{dx_o}\left[\frac{1}{2}+f(x_o,a,n)\right]+f(x_o,a,n)[1+f(x_o,a,n)]. \tag{20}$$

Observe that in the range of the parameters where $f(x_o,a,n)\gg 1$, which is fulfilled when $n \gg 1$, we can keep the second order term in the expansion of $G(w,t,g,\lambda,a,n)$ around the saddle point. Then, we can approximate the double integral in Eq. (15) as follows:

$$S_{Aprox}(g,a,n)=4\pi\frac{\lambda^2(1-\exp(-g/\lambda))}{\sqrt{D[x_o,a,n]}}\exp[G(w_o,t_o,g,\lambda,a,n)]. \tag{21}$$

In the limit $\lambda\to\infty$ we obtain the following approximate expression for $S(g,a,n)$:

$$S_{Aprox}(g,a,n)=\sqrt{2\pi}e^{-1/2}\frac{\sqrt{f[x_o,a,n]+1}}{\sqrt{D[x_o,a,n]}}[x_o]^{n+1}H[x_o,a]\exp[-f[x_o,a,n]]. \tag{22}$$

Note that Eq. (22) is valid for functions $H(x,a)$ that fulfill the following general conditions. First, the relationship given by Eq. (18) must be biunivocal. Second, $D(x_o,a,n)$ must be positive at x_o. Third, $f(x_o,a,n)$ must be larger than one. These conditions provide the range of values of the parameters where the approximate solution, Eq. (22), is valid.

Finally, we replace Eq. (22) into Eq. (11) to obtain an approximate analytical expression for the Laplace transform $S(g,a)$. In particular, in the limit $n\to\infty$, we obtain the following analytical solution for $S(g,a)$:

$$S(g,a)=\lim_{n\to\infty}(-)^n\underbrace{\int dg\cdots\int dg}_{n}S_{Aprox}(g,a,n). \tag{23}$$

One particular case of this result is the one where $H(x,a)$ does not contribute to the saddle point. This is the case when $f(x_o,a,n)$ can be approximated by $1+n$ [the derivative of $\ln(H(x_o,a))$ is negligible]. Then, the saddle point solution is $x_o(g,a,n)\simeq(n+\frac{3}{2})/g$ and the expression of $S_{Aprox}(g,a,n)$ is

$$S_{Aprox}(g,a,n)\simeq\frac{\Gamma(n+1)}{g^{n+1}}H[x_o(g,a,n),a],\quad n\gg 1. \tag{24}$$

Another important property of the expression given by Eq. (23) is that, in the limit $n\to\infty$, the approximate solution, Eq. (22), becomes an exact solution for Eq. (9). Thus, as long as the n indefinite integrals are calculated without approximations, then Eq. (23) is an exact solution for Eq. (7).

In summary, the procedure to use the GBT to compute Fourier sine transforms is the following. First, one has to solve the implicit equation, Eq. (18), for $n\gg 1$ to obtain the mathematical expression of $x_o(g,a,n)$. Replacing this expression into Eq. (22) and doing the n indefinite integrals in Eq. (23), we get the expression for $S(g,a)$. Finally, one has to compute the analytic continuation of $S(g,a)$, Eq. (8), to get the solution of the Fourier sine transform, Eq. (6).

In the next section we apply this technique to compute exactly the polymer propagator of flexible macromolecules.

III. APPLICATION TO THE RANDOM FLIGHT MODEL OF FLEXIBLE POLYMERS

Let us start by analyzing the polymer propagator predicted by the random flight model which is given by Eq. (1). Using the Fourier representation of the delta function,[9] we obtain

$$\begin{aligned}P(\mathbf{R},n)&=\int\frac{d^3k\exp(-i\mathbf{R}\cdot\mathbf{k})}{(2\pi)^3(4\pi l^2)^n}\left[\int d\{\mathbf{R}_k\}\prod_{j=1}^{n}\delta(|\mathbf{R}_j|-l)\exp\left(i\sum_{j=1}^{n}\mathbf{R}_j\cdot\mathbf{k}\right)\right]\\&=\int\frac{d^3k}{(2\pi)^3}\exp(-i\mathbf{R}\cdot\mathbf{k})K(\mathbf{k},n,l),\end{aligned} \tag{25}$$

where the characteristic function, $K(\mathbf{k},n,l)$, is

$$K(\mathbf{k},n,l)=\left(\frac{\sin(|\mathbf{k}|l)}{|\mathbf{k}|l}\right)^n. \tag{26}$$

The evaluation of the angular integrals in Eq. (25) is straightforward. After rescaling $\mathbf{R}$ and $\mathbf{k}$ with the Kuhn length, l, we obtain the final expression for the polymer propagator

$$P(R,n)=\frac{2}{(2\pi)^2R}\int_0^\infty dk\left[\sin(kR)\left(\frac{\sin(k)}{k}\right)^n k\right], \tag{27}$$

where $k=|\mathbf{k}|$ and $R=|\mathbf{R}|$.

This integral representation of the polymer propagator is a Fourier sine transform and can be solve exactly using GBT. Then, our first step consists of expressing the polymer propagator, Eq. (27), in terms of a Laplace transform. For this purpose we define the function

$$S(b,n)\equiv\int_0^\infty dw\left[\exp(-wb)\left(\frac{\sin(w)}{w}\right)^n w\right], \tag{28}$$

from where we recover the expression of the polymer propagator, Eq. (27), as the analytic continuation of the function $S(b,n)$ to the complex plane

$$P(R,n)=\frac{2}{(2\pi)^2R}\,\mathrm{Im}\{S(b=-iR,n)\}. \tag{29}$$

Let us now rewrite Eq. (28) as follows:

$$S(b,n)=\frac{\partial^n}{\partial c^n}\left\{\int_0^\infty dw\left[w\exp(-wb)\exp\left(c\frac{\sin(w)}{w}\right)\right]\right\}_{c=0}=\frac{\partial^n}{\partial c^n}\{GA(b,c)\}_{c=0}, \tag{30}$$

where

$$GA(b,c)\equiv\int_0^\infty dww\exp(-wb)H(w,c), \tag{31}$$

and

$$H(w,c)\equiv\exp\left[c\frac{\sin(w)}{w}\right]. \tag{32}$$

Then, the integral expressed by Eq. (31) satisfies all the requirements of the GBT technique.[7] Consequently, we evaluate this integral in the following way:

$$GA(b,c)=\lim_{N\to\infty}(-)^N\underbrace{\int db\cdots\cdots\cdots\int}_{N}dbS(b,c,N), \tag{33}$$

where we have defined

$$S(b,c,N)\equiv\int_0^\infty dw[w^{N+1}\exp(-wb)H(w,c)]. \tag{34}$$

In the asymptotic limit of $N\to\infty$, the GBT provides an analytical solution for Eq. (34). Following the technique, we first solve the following implicit equation for w_o, Eq. (18),

$$\left\{N+1+w_o\frac{\partial}{\partial w_o}\ln[H(w_o,c)]\right\}\left\{N+2+w_o\frac{\partial}{\partial w_o}\ln[H(w_o,c)]\right\}=w_o^2b^2, \tag{35}$$

whose asymptotic solution is

$$w_o\simeq\frac{N+5/2}{b}N\gg 1. \tag{36}$$

Replacing this expression for w_o in the expression provided by the GBT, Eq. (22), we obtain

$$S(b,c,N) \simeq \frac{\Gamma(N+2)}{b^{N+2}} H\left(\frac{N+5/2}{b},c\right), \quad N \gg 1. \tag{37}$$

Furthermore, we place Eq. (37) into Eq. (33) and the resulting expression into Eq. (30), then we obtain

$$S(b,n) = \lim_{c\to 0} \frac{\partial^n}{\partial c^n} \left\{ \lim_{N\to\infty} (-)^N \underbrace{\int db \cdots\cdots\cdots \int}_{N} db \frac{\Gamma(N+2)}{b^{N+2}} H\left(\frac{N+5/2}{b},c\right) \right\}. \tag{38}$$

We now proceed to exchange the order of the operators; first we evaluate the nth derivative of the function H with respect to c and, afterward, we take the limit of $c \to 0$. As a result, we obtain

$$S(b,n) = \lim_{N\to\infty} (-)^N \int db \cdots \int db \frac{\Gamma(N+2)}{b^{N+2}} \left(\frac{\sin(N/b)}{N/b}\right)^n. \tag{39}$$

Next, we solve the N integrations. Using properties of the function $\sin(x)$ we can write $S(b,n)$ for any odd number of segments as follows:

$$S(b,n) = \frac{1}{2^{n-1}} \sum_{k=0}^{(n-1)/2} (-)^{(n-1)/2+k} \binom{n}{k} M(N,n,k,b), \tag{40}$$

where

$$M(N,n,k,b) \equiv \lim_{N\to\infty} (-)^N \operatorname{Im} \sum_{r=0}^{\infty} \frac{(i(n-2k))^r N^{r-n}}{r!} \int db \cdots \int db \frac{\Gamma(N+2)}{b^{N+2-n+r}}. \tag{41}$$

We note that the only powers of b in Eq. (41) that fulfill the asymptotic behavior of the function $S(b,n)$, Eq. (12), are those that satisfy the condition $r \geqslant (n-1)$. Consequently, the N indefinite integrations are exactly doable; the result is

$$\int db \cdots \int db \frac{1}{b^{N+2-n+r}} = \frac{\Gamma(2+r-n)}{\Gamma(N+2-n+r)} \frac{(-)^N}{b^{2+r-n}}. \tag{42}$$

Placing Eq. (42) into Eq. (41) and introducing the dummy variable $r = x+n-1$ we can write

$$M(N,n,k,b) \equiv \operatorname{Im} \frac{1}{b} (i(n-2k))^{n-1} \sum_{x=0}^{\infty} \left(\frac{i(n-2k)}{b}\right)^x \frac{\Gamma(x+1)}{\Gamma(x+n)} \times \lim_{N\to\infty} \frac{N^{x-1}\Gamma(N+2)}{\Gamma(N+x+1)}, \tag{43}$$

which, after using the asymptotic properties of the gamma function,[13]

$$\lim_{N\to\infty} \frac{N^{x-1}\Gamma(N+2)}{\Gamma(N+x+1)} = 1, \tag{44}$$

becomes

$$M(n,k,b) = \frac{1}{b} \operatorname{Im} \sum_{x=0}^{\infty} (i(n-2k))^{n-1} \left(\frac{i(n-2k)}{b}\right)^x \frac{\Gamma(x+1)}{\Gamma(x+n)}. \tag{45}$$

The sum over x is doable, the result gives the following expression for $M(n,k,b)$,

$$M(n,k,b)=\frac{1}{b}\,\mathrm{Im}[(i(n-2k))^{n-1}FD(n,k,b)], \tag{46}$$

where we have defined

$$FD(n,k,b)\equiv\frac{\Gamma(\frac{1}{2})\,{}_3F_2([1,1,\frac{1}{2}],[(n+1)/2,\,n/2],-(n-2k)^2/b^2)}{\sqrt{\pi}\,\Gamma(n)}+\frac{i(n-2k)}{b}\,\frac{{}_3F_2([1,1,\frac{3}{2}],[(n+1)/2,\,(n+2)/2],-(n-2k)^2/b^2)}{\Gamma(n+1)}. \tag{47}$$

${}_3F_2([,,],[,],x)$ is the generalized hypergeometric function.[14] From Eq. (46) we can see that the imaginary part affects only the function $FD(n,k,b)$. Thus, we obtain the final expression for $S(b,n)$

$$S(b,n)=\sum_{k=0}^{(n-1)/2}(-)^k\binom{n}{k}\frac{(n-2k)^n\,{}_3F_2([1,1,\frac{3}{2}],[(n+1)/2,\,(n+2)/2],-(n-2k)^2/b^2)}{b^2 2^{n-1}\Gamma(n+1)}. \tag{48}$$

The last step to obtain the analytical expression of the polymer propagator consists of inserting Eq. (48) into Eq. (29) and computing the analytic continuation of the resulting expression to the complex plane through the substitution $b=-iR$. After doing these computations, we arrived at the following expression for the polymer propagator,

$$P(R,n)=\frac{1}{2^n\pi^2R^3}\sum_{k=0}^{(n-1)/2}(-)^{k+1}\binom{n}{k}(n-2k)^n\frac{1}{\Gamma(n+1)}\times\mathrm{Im}\left\{{}_3F_2\left(\left[1,1,\frac{3}{2}\right],\left[\frac{n+1}{2},\frac{n+2}{2}\right],\frac{(n-2k)^2}{R^2}\right)\right\}. \tag{49}$$

This expression can be simplified even further if we use the well known analytical properties of the hypergeometric function[14] ${}_3F_2(z)$, which is an analytic function for values of $|z|<1$ and its continuation to the rest of complex plane generates one cut on the positive real axis starting at $\mathrm{Re}(z)=1$. This implies that only values of $(n-2k)^2/R^2\geqslant 1$ will contribute to the imaginary part of ${}_3F_2(z)$. Consequently, this condition reduces the number of terms in the k-sum such that the last term of Eq. (49) is $k=[(n-R)/2]$.

The explicit evaluation of $\mathrm{Im}\{{}_3F_2([1,1,\frac{3}{2}],[(n+1)/2,\,(n+2)/2],\,(n-2k)^2/R^2)\}$ can be found in the Appendix. The final expression is

$$\mathrm{Im}\left\{{}_3F_2\left(\left[1,1,\frac{3}{2}\right],\left[\frac{n+1}{2},\frac{n+2}{2}\right],\frac{(n-2k)^2}{R^2}\right)\right\}=-\frac{R^2\pi}{2(n-2k)^n}\frac{\Gamma(n+1)}{\Gamma(n-1)}[n-2k-R]^{n-2},\quad n\geqslant 2. \tag{50}$$

Finally, we place Eq. (50) into Eq. (49) to obtain the exact expression for the polymer propagator:

$$P(R,n)=\frac{1}{2^{n+1}\pi R}\sum_{k=0}^{[(n-R)/2]}(-)^k\binom{n}{k}\frac{[n-2k-R]^{n-2}}{\Gamma(n-1)}. \tag{51}$$

Equation (51) is valid for an odd number of segments, but it is extended to polymers with any number of segments larger than two via analytic continuation. Therefore, we have obtained the well-known[15,16] exact analytical expression for the polymer propagator of flexible chains, Eq. (27), with any number of segments, n, and any end-to-end distance, R.

Observe that Eq. (51) can be used to describe the statistical properties of polymers with other topologies. For example, consider the case of a flexible m-arm star polymer as shown in Fig. 1. Since the polymer is flexible, then each arm behaves independently from the other ones except for the fact that all of them start at the origin. Thus, the probability of finding the end of the jth arm in the shell of radius R_j with thickness dR_j centered at the origin is

$$4\pi R_j^2 P(R_j, n_j) dR_j, \tag{52}$$

where n_j is the number of segments in the jth arm. If we consider all the arms, then the probability of finding the end of the first, second, etc. arms in the shells of radii R_1, R_2, etc. with thicknesses dR_1, dR_2, etc. centered at the origin is

$$(4\pi)^m \prod_{j=1}^{m} R_j^2 P(R_j, n_j) dR_j. \tag{53}$$

Other probability distributions for star polymers can also be computed easily.

Another example is the case of ring (cyclic) polymers. Figure 1 shows this topology. From this figure and following the steps presented in this article for linear polymers, it can be proved that the probability of finding any pair of segments separated by a distance R should be proportional to the product of two propagators of the form given by Eq. (51),

$$P_{Ring}(R,s,n-s) \propto P(R,s)\ P(R,n-s), \tag{54}$$

where n is the total number of segments in the ring and s is the number of segments (along the contour of the polymer chain) between the two chosen segments.

The aforementioned two examples clearly show that the results obtained for linear polymers using the GBT can be used for polymers with other topologies, thus increasing the number of models that are mathematically tractable with the GBT.

IV. CONCLUSIONS

In this article we have described a new mathematical method called the generalized Borel transform and applied it to compute some statistical properties (polymer propagator) of models of flexible polymers. Specifically, we showed how the GBT was constructed and how to use it to compute Mellin/Laplace transforms. Moreover, some mathematical properties were presented. The application of this technique to the statistical mechanics of single flexible polymers led to the exact solution for the polymer propagator of linear polymers. The propagator obtained turned out to be a finite sum of polynomials valid for any end-to-end distance, R, and number of segments, n. Furthermore, this result was used to compute distribution functions for two other topologies, rings and stars.

The exact computation of the polymer propagator of the RFM is a straightforward calculation that requires simple mathematics when the GBT is used. Indeed, the GBT requires basic elements of calculus and complex variables. This mathematical simplicity of the technique makes it a potentially very useful computational tool for more complex models of single polymer chains because it does not add any complexity to the physics of the starting model.

Equation (51) together with its extensions to stars and rings, Eqs. (53) and (54), and the discussion presented in the Introduction show that the GBT can solve exactly a wide range of models for polymers. However, more advanced models of single polymer chains like the wormlike chain model or helical polymers[5] where the bond vectors are correlated with each other through potential interactions are not exactly solvable with the GBT at present. This is a consequence of the fact that the characteristic function of these models is not known exactly.[5] This function is a Fourier sine transform in $3n$ dimensions. Thus, a generalization of the GBT to multidimensional integrals is required to address these models.

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APPENDIX: EVALUATION OF $\mathrm{Im}\{{}_3F_2(z)\}$

In this appendix, we calculate the expression $\mathrm{Im}\{{}_3F_2(z)\}$. For this purpose, we use the following integral representation of the hypergeometric function:[17]

$$
\begin{aligned}
{}_3F_2\left(\left[-\nu,\frac{\lambda}{2},\frac{\lambda+1}{2}\right],\left[\frac{\lambda+\mu}{2},\frac{\lambda+\mu+1}{2}\right],-\frac{q^2}{w^2}\right)&=[w^{2\gamma}q^{\lambda+\mu-1}B(\lambda,\mu)]^{-1}\\
&\quad\times\int_0^q x^{\lambda-1}[q-x]^{\mu-1}[x^2+w^2]^{\nu}dx,\\
&\quad\lambda,\mu>0,\quad \mathrm{Re}\left(\frac{q}{w}\right)>0,
\end{aligned}
\tag{A1}
$$

where $B(\lambda,\mu)$ is the Beta function.[17]

We now assign the values $\nu=-1$, $\lambda=2$, $\mu=n-1$, $q=n-2k$, and $w=b$ to the parameters in Eq. (A1) to obtain

$$
\begin{aligned}
&{}_3F_2\left(\left[1,1,\frac{3}{2}\right],\left[\frac{n+1}{2},\frac{n+2}{2}\right],-\frac{(n-2k)^2}{b^2}\right)\\
&\quad=\frac{1}{b^{-2}(n-2k)^nB(2,n-1)}\int_0^{n-2k}x[n-2k-x]^{n-2}[x^2+b^2]^{-1}dx.
\end{aligned}
\tag{A2}
$$

This integral representation is valid only for $n\geqslant 2$. Therefore, when we take the analytic continuation to the complex plane $(b=-iR)$, we can express the imaginary part of the hypergeometric function as follows:

$$
\begin{aligned}
&\mathrm{Im}\left\{{}_3F_2\left(\left[1,1,\frac{3}{2}\right],\left[\frac{n+1}{2},\frac{n+2}{2}\right],\frac{(n-2k)^2}{R^2}\right)\right\}\\
&\quad=-\frac{R^2}{(n-2k)^nB(2,n-1)}\,\mathrm{Im}\int_0^{n-2k}x[n-2k-x]^{n-2}[x^2-R^2]^{-1}dx.
\end{aligned}
\tag{A3}
$$

Thus, we need to evaluate

$$
L\equiv\mathrm{Im}\int_0^{n-2k}x[n-2k-x]^{n-2}[x-R]^{-1}[x+R]^{-1}dx.
\tag{A4}
$$

After analyzing the analytical behavior of the integrand, we concluded that we can exchange the operations of integration and imaginary part to obtain

$$
L=\int_0^{n-2k}x[n-2k-x]^{n-2}[x+R]^{-1}\,\mathrm{Im}\{[x-R]^{-1}\}dx.
\tag{A5}
$$

Thus, we have to compute

$$
LS=\mathrm{Im}\left\{\frac{1}{(x-R)}\right\},
\tag{A6}
$$

first and, afterward, we have to solve the integral given by Eq. (A5).

The analytical behavior of the function $(x-R)^{-1}$ is well known. It is an analytic function for $|x|>R$ but, its analytic continuation to the complex plane generates a cut on the real axis in the range $-R<\mathrm{Re}(x)<R$. This cut generates its imaginary part, which is

$$\mathrm{Im}\left\{\frac{1}{(x-R)}\right\}=\pi\delta(x-R). \tag{A7}$$

Thus, placing Eq. (A7) into Eq. (A5) and making the change of variables $y=x-R$, we obtain

$$L=\pi\int_{-R}^{n-2k-R}F_k(y,n,R)\,\delta(y)\,dy, \tag{A8}$$

where

$$F_k(y,n,R)\equiv(y+R)[n-2k-R-y]^{n-2}[y+2R]^{-1}. \tag{A9}$$

The result of the integration gives

$$L=\frac{\pi}{2}[n-2k-R]^{n-2}. \tag{A10}$$

Finally, we place Eq. (A10) into Eq. (A3) to obtain the final expression

$$\mathrm{Im}\left\{{}_3F_2\left(\left[1,1,\frac{3}{2}\right],\left[\frac{n+1}{2},\frac{n+2}{2}\right],\frac{(n-2k)^2}{R^2}\right)\right\}=-\frac{\pi}{2}\,\frac{R^2}{(n-2k)^n B(2,n-1)}[n-2k-R]^{n-2}. \tag{A11}$$

[1] K. F. Freed, *Renormalization Group Theory of Macromolecules* (Wiley, New York, 1987).
[2] W. Kuhn, Kolloid-Z. **68**, 2 (1934).
[3] H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971).
[4] W. L. Mattice and U. W. Suter, *Conformational Theory of Large Macromolecules: The Rotational Isomeric State Model in Macromolecular Systems* (Wiley, New York, 1994).
[5] H. Yamakawa, *Helical Worm-like Chains in Polymer Solutions* (Springer, Berlin, 1997).
[6] L. N. Epele, H. Fanchiotti, C. A. Garcia Canal, and M. Marucho, Phys. Lett. B **523**, 102 (2001).
[7] L. N. Epele, H. Fanchiotti, C. A. Garcia Canal, and M. Marucho, Phys. Lett. B **556**, 87 (2003).
[8] L. N. Epele, H. Fanchiotti, C. A. Garcia Canal, and M. Marucho, Nucl. Phys. B **583**, 454 (2000).
[9] G. Arfken, *Mathematical Methods for Physicists* (Academic, New York, 1985).
[10] N. Bleistein and R. Handelsman, *Asymptotic Expansion of Integrals* (Dover, New York, 1986).
[11] E. T. Copson, *Asymptotic Expansions* (Cambridge University Press, Cambridge, 1965).
[12] H. Jeffrey and B. S. Jeffrey, *Methods of Mathematical Physics* (Cambridge University Press, Cambridge, 1966).
[13] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1970).
[14] H. Bateman, *Higher Transcendental Functions* (McGraw–Hill, New York, 1953).
[15] M. C. Wang and E. Guth, J. Chem. Phys. **20**, 1144 (1952).
[16] C. Hsiung, H. Hsiung, and A. Gordus, J. Chem. Phys. **34**, 535 (1961).
[17] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 2000).