Elastic response of the Dirac chain

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The elastic response to elongation forces is studied for polymer chains of arbitrary stiffness using a recently discovered relation between semiflexible polymers and Euclidean Dirac fermions. We obtain elongation as a function of an external force and an elastic force as a function of elongation for polymer chains of arbitrary stiffness. We also obtain the elastic moduli for such chains. The obtained results represent a first step towards development of the consistent theory of semiflexible polymer networks.

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I. INTRODUCTION

Recently Gaveau and Schulman [1] have studied the response of a Gaussian random coil polymer chain to the applied uniform electric field. Earlier, similar problems were studied in Ref. [2], where the response to the gravitational field has been investigated, and in Ref. [3], where the response to the uniform field was studied in half-space geometry. The authors of Ref. [1] have noticed a pathological behavior of the mean square end-to-end distance $\langle \mathbf{R}^2 \rangle$ in the presence of the electric field $\mathbf{E}$,

$$\langle \mathbf{R}^2 \rangle = lN + \frac{q^2E^2N^4}{4(k_BT)^2} . \tag{1.1}$$

Here l and N are the Kuhn and the full polymer length, respectively, q is the electric charge per monomer, and k_BT is the usual temperature factor. Equation (1.1) implies that for strong enough fields (or low temperatures) $\langle \mathbf{R}^2 \rangle \alpha N^4$, while it is obvious that $\langle \mathbf{R}^2 \rangle$ cannot grow faster than N^2 (i.e., faster than the rigid rod). The pathologies of the Gaussian model could be corrected if a more realistic model describing the conformational properties of polymers could be found. By observing that the Wiener process leading to the Gaussian chain model [4] is the limiting case of the Poissonian process, the authors of Ref. [1] have proposed to replace the Gaussian propagator obtainable as a Green's-function solution of the diffusion equation

$$\frac{\partial}{\partial N} G(\mathbf{r},\mathbf{r}';N) = \frac{l}{6}\nabla^2 G(\mathbf{r},\mathbf{r}';N) + \delta(\mathbf{r},\mathbf{r}')\delta(N) , \tag{1.2}$$

by that coming from the Green's-function solution of the telegrapher equation. The calculations of $\langle \mathbf{R}^2 \rangle$ based on the telegrapher equation have produced $\langle \mathbf{R}^2 \rangle \alpha N^2$ in the strong field regime and, for $E=0$, in the flexible chain limit they have produced $\langle \mathbf{R}^2 \rangle = lN$, as required. The above results indicate that the single chain statistics based on the Wiener measure is dangerous, and may lead to results that are not physically useful.

Probing the response of polymer chains to the external elongating field is very important in the statistical mechanics of polymers, as was emphasized already by de Gennes [5]. The standard example of such importance is the theory of rubber elasticity [6]. The basis for the entropy elasticity for rubberlike materials is in the knowledge of the elongational characteristics of a polymer, which is experiencing action of forces at both ends. Although the theories based on such knowledge are often too simplistic and do not lead to material equations for the macroscopic samples [7,8], they provide a very useful insight into the basic physics of rubber elasticity.

The statistics of Gaussian chains, obtained from the solution of Eq. (1.2), is based on the distribution functions, which provides finite probabilities for unphysical configurations of the chain for which $R > Nl$, $R = |\mathbf{r}-\mathbf{r}'|$. The conformational properties of the finite flexible chains were extensively studied by Kuhn and co-workers [6], and independently by Volkenstein [9]. The common result of their work lies in obtaining the distribution functions, which are zero for all configurations $R > N$. The stretching of such finite chains leads to a singularity of the force at maximum elongation, and the force-extension relationship is described by a Langevin-type function. Simple single finite chain properties were recently discussed in Ref. [10] where the Schrödinger-like theory [based on Eq. (1.2)] has been replaced by the "relativistic" Klein-Gordon (KG) type theory, which had produced the required singularity at maximum elongation.

Various versions of path integrals leading to Klein-Gordon-type theories have been recently discussed by many authors, e.g., see Ref. [11], etc. For the purposes of our presentation, following Polyakov, Ref. [12] and also, Ref. [11], consider the path integral for the KG propagator written in the form

$$G(\mathbf{r},\mathbf{r}';N) = \int D[\mathbf{u}(\tau)]\delta[\mathbf{u}^2(\tau)-1] \times \exp\left\{-\frac{\kappa}{2}\int_0^N d\tau \left[\frac{d\mathbf{u}}{d\tau}\right]^2\right\} \times \delta\left[\mathbf{r}-\mathbf{r}'-\int_0^N d\tau\,\mathbf{u}\right] , \tag{1.3}$$

where $\mathbf{u} = d\mathbf{r}/d\tau$, $\mathbf{r}(\tau)$ is the spatial position of the poly-

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mer segment, which has the contour position τ [4], while κ is the bending rigidity constant. For $N\to\infty$ and κ finite, the Fourier transformed propagator, Eq. (1.3), is found [11] to be

$$G(\mathbf{k},N)=2e^{-C_d\kappa\mathbf{k}^2N}+O(e^{-N/\kappa}) , \tag{1.4}$$

where $C_d=2$ (for $d=2$) and $2/d$ $(d-1)$ for $d\geq 3$, where d is the dimensionality of the Euclidean embedding space. For N finite and κ arbitrary, a systematic $1/d$ expansion can be performed [13], which produces the leading result

$$\langle \mathbf{u}(\tau)\cdot\mathbf{u}(0)\rangle=\exp\left[-\frac{d}{2\kappa}|\tau|\right] \tag{1.5}$$

characteristic for one-dimensional Heisenberg models as discussed in Ref. [14]. While for arbitrary N, the Laplace transform of Eq. (1.4) produces the KG result,

$$G(\mathbf{k},s)\alpha\frac{1}{\mathbf{k}^2+M^2} , \tag{1.6}$$

with $M^2=s/C_d\kappa$, where s is the Laplace variable conjugate to N. Unfortunately, not all conformational properties of semiflexible chains can be adequately described with the help of the propagator just described.

Notice that in Refs. [15] and [16] an observation that the telegrapher equation can be recast in the form of the Dirac equation was extensively used, thus producing, instead of Eq. (1.2), the equation for the Dirac propagator. We have performed extensive studies of the relevance of the Dirac propagator for the calculation of the conformational properties of polymer chains of arbitrary flexibility [17] (including the case of confined geometries, e.g., half space, etc. [18]). The most convincing evidence, so far, of the usefulness of the Dirac propagator for the computation of conformational properties comes from the calculations of the static scattering form factor $S(\mathbf{k})$ performed in Refs. [17,19], and experimentally confirmed in Ref. [20] (references to earlier experimental papers supporting the results of Ref. [19] can be found in the reference list to this work).

Following Ref. [11], the Dirac propagator can be written in the form analogous to Eq. (1.3), i.e.,

$$G^D(\mathbf{r},\mathbf{r}';\mathbf{u}_f,\mathbf{u}_i;N)=\int_{\mathbf{u}(0)=\mathbf{u}_i}^{\mathbf{u}(N)=\mathbf{u}_f}[\mathbf{u}(\tau)]\delta(\mathbf{u}^2-1)\delta\left[\mathbf{r}-\mathbf{r}'-\int_0^N d\tau\,\mathbf{u}\right]\exp\left\{-\frac{\kappa}{2}\int_0^N d\tau\left[\frac{d\mathbf{u}}{d\tau}\right]^2+i\int_0^N d\tau\,\mathbf{A}[\mathbf{u}(\tau)]\cdot\frac{d\mathbf{u}}{d\tau}\right\} . \tag{1.7}$$

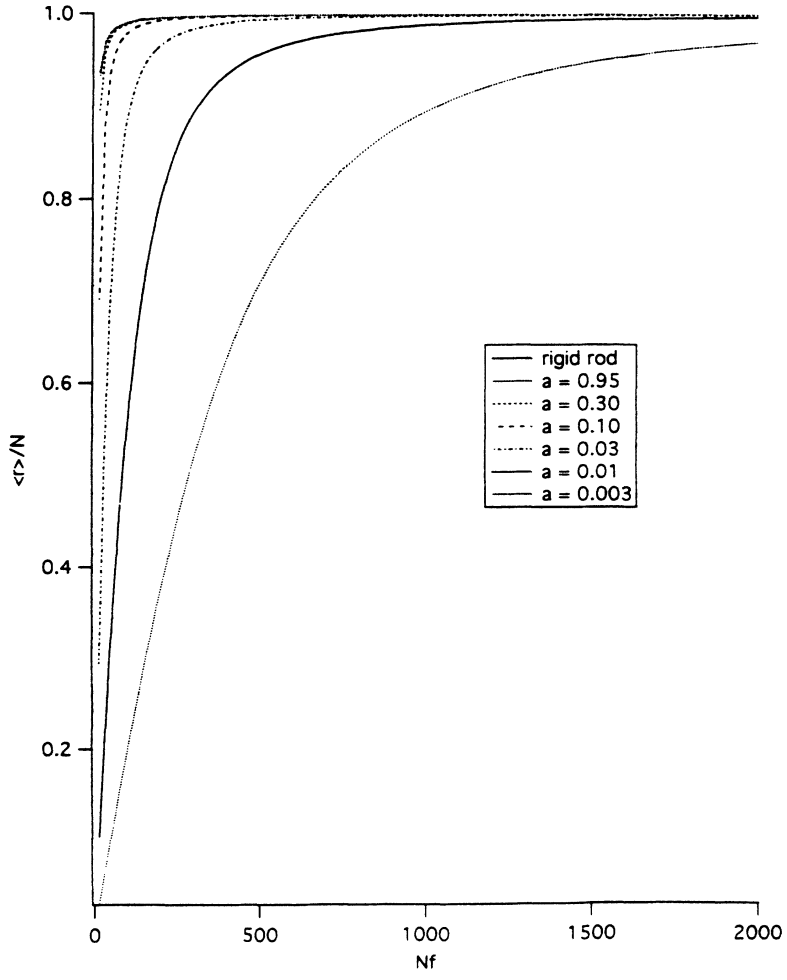

FIG. 1. Elongation $\langle \mathbf{R}\rangle/N$ as function of the external force Nf for polymer chains of representative length $N=40$ and various stiffness constants (e.g., $a=0.01N$, etc.).

The gauge field **A** responsible for the phase (spin) factor given by the second term in the exponent in Eq. (1.7) converts the KG propagator into that for the Dirac particle. The explicit form of the spin factor depends upon d and is given, for example, in Refs. [1,12,21,22]. Because of this factor, it should be noted that, unlike the Gaussian case, the conformational properties of the Dirac chain depend to some extent upon the conformational (spin) states of the chain ends as it is explained in Refs. [14,16], and could be seen directly from Eq. (1.7). For example, if one of the ends is anchored at the wall in a certain conformational state, this will affect the conformation of the whole chain. This is a very plausible property of propagators, especially for polymer liquid crystalline chains, which complements other studies of liquid crystalline ordering in the presence of surfaces [23]. Accordingly, the effects of external forces on the Dirac chain will depend, in general, upon the "polarization state" of its ends. In the present study, we shall consider only the simplest situation of free chain ends for the sake of illustration of main features, of our approach. As in the case of flexible Wiener chains [7], the results of this study are a step in the development of the theory of randomly crosslinked networks of chains of arbitrary flexibility.

In Sec. II we provide some necessary background material needed to formulate the statement of the problem to be solved. In Sec. III we calculate the elastic response of the Dirac chains to the external fields, other than nematic. The results of our calculations are summarized in Figs. 1 and 2. It is remarkable that our calculations involve the Pauli-Jordan function, which is related to the space-time commutator (anticommutator) of the Bose (Fermi) fields in quantum field theories [24] as was first noticed by Dirac [25]. This function is manifestly zero for $R > N$ and produces a Langevin-type function in the force-extension relationship in complete qualitative accord with the earlier results of Kuhn *et al.* [6] and Volkenstein [9]. In Sec. IV we calculate the elastic moduli for Dirac chains, discuss our results, and propose problems for further study.

II. BACKGROUND AND STATEMENT OF THE PROBLEM

In this section the known difficulties of describing semiflexible chains with the use of traditional models are illustrated and the quantities to be calculated are defined. One of the traditional models was introduced in Ref. [26]. This model is found to be useful when its results are compared to experiments for not too stiff chains, i.e., this model effectively represents a "renormalized" Gaussian chain with persistence length larger than for the fully

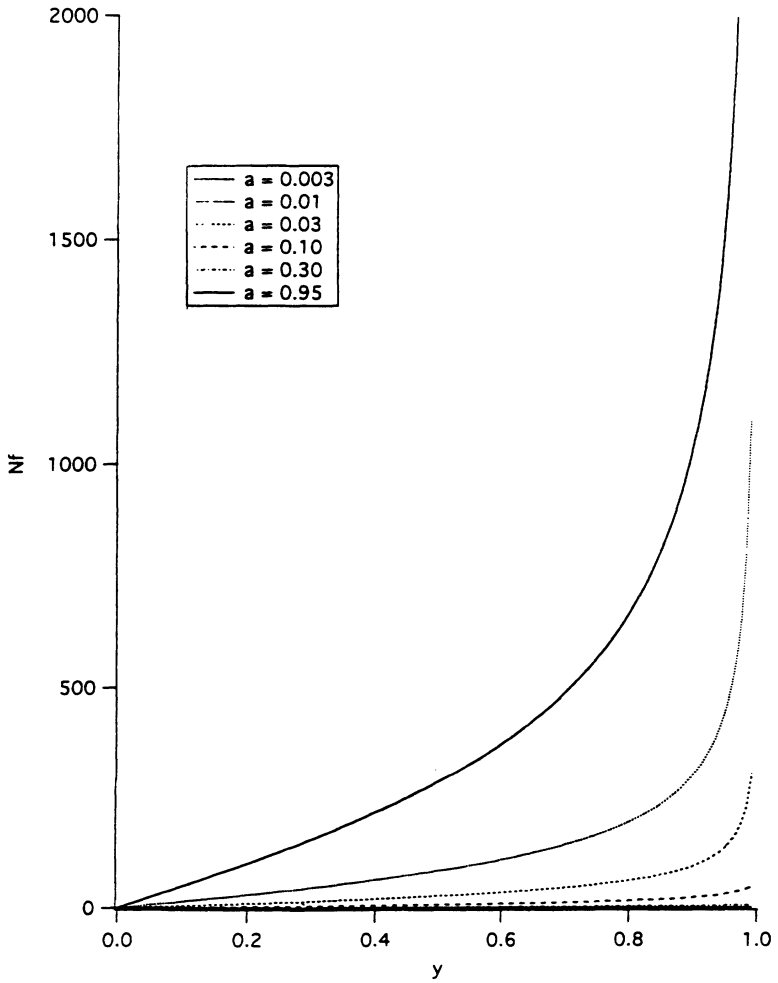

FIG. 2. Force Nf as a function of elongation $y=\langle \mathbf{R} \rangle /N$ for polymer chains of representative length $N=40$ and various stiffness constants (e.g., $a=0.01N$, etc.).

flexible polymers [27,28]. To illustrate some of the basic difficulties, let $G(\mathbf{r},N)$ be the end-to-end distribution function [e.g., see Eq. (1.2)], then, following de Gennes [5], the generating function $Z(\mathbf{f})$ for the chain in the field of force $\mathbf{f}$ is given by

$$Z(\mathbf{f})=\int d\mathbf{R}\, G(\mathbf{R},N)e^{\mathbf{f}\cdot\mathbf{R}} , \tag{2.1}$$

where $\mathbf{f}=\mathbf{F}/k_BT$. If $G(\mathbf{k},N)$ is the Fourier transform of $G(\mathbf{R},N)$, then, obviously, $Z(\mathbf{f})$ is related to $G(\mathbf{k})$ via the replacement $\mathbf{f}\rightleftarrows i\mathbf{k}$. The size of the chain $\langle\mathbf{R}\rangle$ under the action of force is given by

$$\langle\mathbf{R}\rangle=\frac{\partial}{\partial\mathbf{f}}\ln Z(\mathbf{f}) . \tag{2.2}$$

Because $Z(\mathbf{f})=G(-i\mathbf{f},N)$ we obtain as well

$$\langle\mathbf{R}\rangle=\frac{1}{i}\frac{\partial}{\partial\mathbf{k}}\ln G(\mathbf{k},N)=\frac{\partial}{\partial\mathbf{f}}\ln G(-i\mathbf{f},N) . \tag{2.3}$$

We introduce now the Legendre transform via

$$-\langle\mathbf{R}\rangle\cdot\mathbf{f}+\ln Z(\mathbf{f})=\ln W(\langle\mathbf{R}\rangle) , \tag{2.4}$$

so that

$$-\frac{\partial}{\partial\langle\mathbf{R}\rangle}\ln W(\langle\mathbf{R}\rangle)=\mathbf{f} , \tag{2.5}$$

and, obviously, we have also Eq. (2.2).

Equation (2.4) can be understood as follows. Let

$$W(\langle\mathbf{R}\rangle)=\int d\mathbf{f}\, Z(\mathbf{f})e^{-\mathbf{f}\cdot\langle\mathbf{R}\rangle}$$
$$=\int d\mathbf{f}\exp[\ln Z(\mathbf{f})-\mathbf{f}\langle\mathbf{R}\rangle] , \tag{2.6}$$

then, using the saddle point method, i.e., Eq. (2.2), we arrive back at Eq. (2.4). If, for whatever reason, we cannot use the saddle point method (see below), then the results obtained with the help of Eqs. (2.2) and (2.5) may be, in principle, different.

Moreover, even Eq. (2.1) should be treated with some caution. Indeed, at the microscopic level, the force term should be added to the microscopic action functional. In the Gaussian limit, e.g., see Eqs. (1.3) and (1.4), such an addition produces the same final result as Eq. (2.1) does. But, in general, this may not be the case. For example, in the existing theory of directed polymers [29], the total action functional describing interaction with nematic ordering field $\mathbf{n}$ is given by

$$S=\frac{\kappa}{2}\int_0^N d\tau\left[\frac{d\mathbf{u}}{d\tau}\right]^2-g\int_0^N d\tau(\mathbf{u}\cdot\mathbf{n})^2 , \tag{2.7}$$

where g is some coupling constant and the rest of the notations are the same as in Eqs. (1.3) and (1.7). Only after use of the Hubbard-Statonovich transformation applied to the second term in Eq. (2.7), with subsequent use of the saddle point approximation (with respect to the auxiliary field φ, thus making it effectively constant), is it possible to remove the square in the second term in Eq. (2.7), thus, again effectively leading to the result, Eq. (1.4), and, whence, to Eq. (2.1).

In our treatment we shall use only the linear coupling, which produces for both KG, Eq. (1.4), and Dirac, Eq. (1.7), the result, Eq. (2.1), as can be seen from Polyakov's lecture notes, Ref. [12]. The quadratic coupling and, whence, the problem of hairpins [29] will be studied in a separate publication.

Following Ref. [9] consider now a simple example. Let $G(\mathbf{R},N)$ be an arbitrary distribution function (not necessarily that for Gaussian chains), then for small enough forces we can write

$$Z(\langle\mathbf{f}\rangle)=\int d\mathbf{R}\, G(\mathbf{R},N)e^{-\mathbf{f}\cdot\langle\mathbf{R}\rangle}$$
$$=2\pi\int_0^\infty d\mathbf{R}\,\mathbf{R}^2G(|\mathbf{R}|,N)\int_0^\pi d\theta(\sin\theta)e^{fR\cos\theta}$$
$$=\left\langle\frac{\sinh(fR)}{fR}\right\rangle , \tag{2.8}$$

where $\langle\cdots\rangle$ denotes the averaging with help of $G(|\mathbf{R}|,N)$. By expanding $\langle[\sinh(fR)]/fR\rangle$ we obtain

$$\left\langle\frac{\sinh(fR)}{fR}\right\rangle=1+\tfrac{1}{6}\langle fR^2\rangle+\cdots , \tag{2.9}$$

so that

$$\ln Z(\mathbf{f})=\ln(1+\tfrac{1}{6}f^2\langle\mathbf{R}^2\rangle+\cdots)\simeq\frac{f^2}{6}\langle\mathbf{R}^2\rangle . \tag{2.10}$$

Using Eq. (2.2) thus produces

$$\langle\mathbf{R}\rangle=\frac{\mathbf{f}}{3}\langle\mathbf{R}^2\rangle . \tag{2.11}$$

In the case of Gaussian coils $\langle\mathbf{R}^2\rangle=lN$ so that we obtain the familiar result [5]

$$\langle\mathbf{R}^2\rangle=\frac{\mathbf{f}}{3}lN \tag{2.12}$$

or

$$\mathbf{f}=\frac{3\langle\mathbf{R}\rangle}{lN} . \tag{2.13}$$

For the case of Dirac chains, we had obtained before [17,19]

$$\langle\mathbf{R}^2\rangle=\tfrac{4}{3}a^2xL(x) , \tag{2.14}$$

where $x=3N/2a$, $L(x)=\coth x-1/x$ is Langevin's function, and in the limit of Gaussian chains ($a\ll N$), we have obtained $l=2a$ so that, in general, *a is the persistence length.* By combining Eqs. (2.11) and (2.14) we obtain

$$\langle\mathbf{R}\rangle=\frac{\mathbf{f}}{3}\frac{4}{3}a^2xL(x) . \tag{2.15}$$

In the random coil limit we have to put $x\rightarrow\infty$ so that $L(x)\rightarrow 1$ and, whence, we obtain back Eq. (2.12), i.e.,

$$\langle\mathbf{R}\rangle=\frac{\mathbf{f}}{3}2aN=\frac{\mathbf{f}}{3}lN . \tag{2.16}$$

In the rigid rod limit, $L(x)\approx x/3$ and we obtain

$$\langle\mathbf{R}\rangle\simeq\frac{\mathbf{f}}{3}N^2 . \tag{2.17}$$

This result is not physically illuminating because it does not reflect the fact that for $\langle\mathbf{R}\rangle/N\rightarrow 1-$ we should have $f\rightarrow\infty$. This is not too surprising in view of Eq. (2.10),

which represents exactly the Gaussian "approximation" for stiff chains which is, of course, physically meaningless. Because of this, consider yet another example. For the case of rigid rods, $G(\mathbf{k},N)$ is known to be [19] $G(\mathbf{k},N)=[\sin(kN)]/kN$ while $G(\mathbf{R},N)$ is given by $G(\mathbf{R},N)=c\delta(\mathbf{R}^2-N^2)$, where the constant c is to be fixed below. To this purpose we write

$$G(\mathbf{k},N)=c\int d\mathbf{r}\,\delta(\mathbf{r}^2-N^2)e^{-i\mathbf{k}\cdot\mathbf{r}}$$
$$=\frac{2\pi c}{k}\int_0^\infty dr^2\delta(r^2-N^2)\sin k\sqrt{r^2}=\frac{2\pi c}{k}\sin kN\ . \tag{2.18}$$

Equation (2.18) produces at once $c=1/2\pi N$ in accordance with Ref. [30]. On the other hand, we have

$$G(\mathbf{R},N)=\int\frac{dk}{(2\pi)^3}e^{-i\mathbf{k}\cdot\mathbf{R}}\frac{\sin kN}{kN}$$
$$=\frac{4\pi}{(2\pi)^3}\int_0^\infty dk\,k^2\frac{\sin R}{kR}\frac{\sin N}{kN}$$
$$=\frac{1}{4\pi NR}[\delta(\mathbf{R}-N)-\delta(\mathbf{R}+N)]\ . \tag{2.19}$$

This result, apparently, contradicts the form of $G(\mathbf{R},N)$ given above. Nevertheless, the calculations are done correctly as can be seen from Ref. [31] [Sec. 5.3, Eqs. (5.32) and (5.35)]. Let us analyze why this is so. For this purpose we have to study more carefully Eq. (2.18),

$$\text{Eq. (2.18)}\propto\int d\mathbf{R}\,\delta(\mathbf{R}^2-N^2)e^{i\mathbf{k}\cdot\mathbf{R}}$$
$$\propto\int d\mathbf{R}\,e^{i\mathbf{k}\cdot\mathbf{R}}\frac{1}{R}\delta(R+N)$$
$$+\int d\mathbf{R}\frac{1}{R}e^{i\mathbf{k}\cdot\mathbf{R}}\delta(R-N)$$
$$\propto\int_0^\infty dR\frac{\sin(kR)}{k}\delta(R-N)\ . \tag{2.20}$$

The above result indicates that if we would start with three different distributions

$$\frac{1}{2\pi N}\delta(R^2-N^2)=\frac{1}{2\pi N}\frac{1}{2r}[\delta(R-N)+\delta(R+N)]\ , \tag{2.21a}$$

$$\frac{1}{4\pi NR}[\delta(R-N)-\delta(R+N)]\ , \tag{2.21b}$$

$$\frac{1}{4\pi NR}\delta(R-N)\ , \tag{2.21c}$$

the final result, Eq. (2.20), would be the same, i.e., the same result, $\langle[\sin(kN)]/kN\rangle$, corresponds to three different distributions. Physically this does not change anything because only $\delta(\mathbf{R}-N)$ will contribute to the final result anyway. But the above example indicates that, *in general*, $G(\mathbf{k},N)$ and $G(\mathbf{R},N)$ may produce *different* analytical dependencies of $\mathbf{f}$ on $\langle\mathbf{R}\rangle$ (or $\langle\mathbf{R}\rangle$ on $\mathbf{f}$) so that the direct, Eq. (2.5), and the inverse, Eq. (2.2), methods may, *in principle*, produce different results.

Below we demonstrate explicitly that, fortunately, that is not the case (at least for Dirac-like chains).

III. CALCULATION OF THE ELASTIC RESPONSE FOR THE DIRAC CHAINS

In Refs. [17,19] we have obtained the closed analyze form for the Dirac propagator in $\mathbf{k}$ space

$$G(\mathbf{k},N)=\frac{m}{\sqrt{\mathbf{k}^2-m^2}}\sin\left[\sqrt{\mathbf{k}^2-m^2}N\right]\ , \tag{3.1}$$

where the inverse rigidity parameter $m=3/2a$ (in three dimensions). The use of Eqs. (2.1) and (2.3) allows us to rewrite Eq. (3.1) in the form useful for computation of the elastic response

$$G(-i\mathbf{f},N)=\frac{mN}{E}\sinh E\ , \tag{3.2}$$

where $E=N\sqrt{\mathbf{f}^2+m^2}$. According to Eqs. (2.2) and (2.3), we obtain now

$$\langle\mathbf{R}\rangle=\frac{\partial}{\partial\mathbf{f}}\ln G(-i\mathbf{f},N)=\frac{N^2\mathbf{f}}{E}L(E)\ , \tag{3.3}$$

where $L(x)$ was defined in Eq. (2.14).

Consider two limiting cases of Eq. (3.3) first. In the limit of rigid rods, $m=0$ and Eq. (3.3) acquires the form

$$\frac{\langle\mathbf{R}\rangle}{N}=L(\mathbf{f}N)\ . \tag{3.4}$$

This form has a correct limiting physical behavior as discussed in the Introduction: for infinitesimally small m, it takes an infinite force to stretch an already rigid chain. The asymptotic form of the result, Eq. (3.4), is also in accord with the findings of Ref. [1] [e.g., see Eq. (1.7) of Ref. [1]].

It is also illuminating to present Eq. (3.4) in the equivalent form by formally inverting the Langevin's function. We obtain in this case

$$\frac{1}{N}L^{-1}\left[\frac{\langle\mathbf{R}\rangle}{N}\right]=\mathbf{f}\ , \tag{3.5}$$

for $N=\langle\mathbf{R}\rangle$ the only solution for $\mathbf{f}$ is $\mathbf{f}=\infty$ [9], which is in accord with our expectations.

Consider now the opposite limit, $m\to\infty$. In this case we obtain

$$\langle\mathbf{R}\rangle\simeq\frac{Nf}{m}=\frac{2aN}{3}\mathbf{f}\ . \tag{3.6}$$

This result coincides with Eq. (2.12) if we write $2a=l$. The identification $2a=l$ in the limit $m\to\infty$ was already discussed in our earlier paper, Ref. [17]. For chains of arbitrary rigidity, Fig. 1 demonstrates the elongation $\langle\mathbf{R}\rangle/N$ as a function of the applied force $\mathbf{f}N$ according to Eq. (33).

It is interesting to observe that for random coils in the strong elongation regime, the usefulness of Gaussian-like

propagator $G_0(\mathbf{k},N)=\exp(-k^2Nl/6)$ was questioned rather long before the work by Gaveau *et al* [15].

In the books by Volkenstein [9] and Treloar [6] the reader may find a very complete summary of the earlier efforts to study the elastic responses of random flight chains. These more accurate calculations have produced a remarkable result for random flight coils:

$$\frac{\langle \mathbf{R} \rangle}{N}=L(\mathbf{f}l)\ , \tag{3.7}$$

where $l=2a$. Equations (3.3) and (3.7) are different in general but in the limit of strong elongations (large force) Eqs. (3.7) and (3.4) practically coincide in complete accord with the requirements discussed in the Introduction.

The results just obtained allow us to determine the elongation under the influence of the external force for chains of arbitrary flexibility. In our previous work, Ref. [17], we have argued that by choosing carefully the rigidity of the chain it is always possible to mimic the effects caused by the excluded volume. Figure 1 provides an additional support to this claim when it is compared with Fig. 1.11 of the de Gennes book [5]. At the same time, it is often of interest to study the conjugate problem: when the chains are already stretched, what is the strength of the elastic force which they exert? To answer this question we have to find an inverse Fourier transform of the Dirac propagator, Eq. (3.1). Fortunately, this task was accomplished by Dirac himself [25] so that here we provide some missing details of his calculations for completeness and the reader's convenience.

We begin by writing

$$\frac{G(\mathbf{R},N)}{m}=\int \frac{d^3k}{(2\pi)^3}e^{i\mathbf{k}\cdot\mathbf{R}}\frac{\sin\left[N\sqrt{\mathbf{k}^2-m^2}\right]}{N\sqrt{\mathbf{k}^2-m^2}}$$
$$=\frac{4\pi}{(2\pi)^3}\int_0^\infty dk\,k^2\frac{\sin R}{kR}\frac{\sin N\sqrt{k^2-m^2}}{N\sqrt{k^2-m^2}}\ . \tag{3.8}$$

For $m=0$, i.e., in the rigid rod limit, we have already discussed the right-hand side (rhs) of Eq. (3.8) earlier, e.g., see Eq. (2.18). Therefore, in the rest of our calculations we shall only study the case when $m\neq 0$.

It is important to realize that for $m\to im$ and $N\to t$ (where t is time) the above defined function G/mN coincides with the Pauli-Jordan function for the commutator (anticommutator) of quantum fields in the Minkowski space time [24]. The fact that the left-hand side of Eq. (3.8) is divided by mN is also important because if we multiply both sides by m, then Eq. (3.8) coincides with a trace of Dirac propagator, as already was noticed by Dirac [25]. Without such multiplication the rhs of Eq. (3.8) and, accordingly, Eq. (3.1), is jut the retarded Green's function for the KG propagator [24]. As we have mentioned earlier, in Ref. [10], the KG propagator was discussed for semiflexible chains. Unfortunately, it cannot be used in general because it will not be able to reproduce correctly the rigid rod limit, e.g., see Eq. (2.19), as shown already in Ref. [17]. In addition, the KG propagator cannot take properly into account the orientation of chain ends, which could sometimes be important [23] as we have mentioned in the Introduction. Following Dirac, let us consider the following chain of transformations given below:

$$\text{Eq. (3.8)}=\frac{2}{(2\pi)^2}\frac{1}{2i}\frac{1}{R}\left[\int_0^\infty\frac{dk\,k}{k_0}(e^{i(kR+Nk_0)}-e^{-i(kR-Nk_0)})-(e^{i(kR-Nk_0)}-e^{-i(kR+Nk_0)})\right]$$
$$=\frac{1}{R}\frac{1}{(2\pi)^2}\frac{1}{(2i)^2}\left[\int_{-\infty}^\infty\frac{dk\,k}{k_0}e^{i(kR+Nk_0)}-\int_{-\infty}^\infty\frac{dk\,k}{k_0}e^{i(kR-Nk_0)}\right]\ , \tag{3.9}$$

where $k_0=\sqrt{\mathbf{k}^2-m^2}$. The above expression differs from that used by Dirac only because in the present case $m^2\to -m^2$. Let us write as well, $m\to im$ and at the end of our calculations we shall go back to our original m. The legitimacy of this procedure is going to be demonstrated below. For $m\Longrightarrow im$ we obtain $k_0=\sqrt{\mathbf{k}^2+m^2}$ and, therefore, Eq. (3.9) can be rewritten as follows:

$$\text{Eq. (3.9)}=\frac{1}{(2\pi)^2}\frac{1}{(2i)^2}\frac{1}{R}\frac{1}{i}\frac{\partial}{\partial R}[I_1-I_2]\ , \tag{3.10}$$

where

$$I_1=\int_{-\infty}^\infty\frac{dk}{k_0}e^{i(kR+Nk_0)}\ ,\quad I_2=\int_{-\infty}^\infty\frac{dk}{k_0}e^{i(kR-Nk_0)}\ . \tag{3.11}$$

Let now $k=m\sinh\varphi$ so that $k_0^2=m^2\cosh^2\varphi$ and, therefore, $k_0=m\cosh\varphi$. Because $dk=m\cosh\varphi\,d\varphi$ we obtain $dk/k_0=d\varphi$. Consider now an integral

$$I=\int_{-\infty}^\infty d\varphi\,e^{im(R\sinh\varphi+X_0\cosh\varphi)}\ , \tag{3.12}$$

where $X_0=\pm N$. Let now $R<N$ (the case $R>N$ can be also considered but it does not have physical meaning for our problem as we shall demonstrate shortly), then if $X_0>0$, let $X_0=\sqrt{\lambda}\cosh\varphi_0$, $R=\sqrt{\lambda}\sinh\varphi_0$ so that

$$\left[\frac{X_0}{\sqrt{\lambda}}\right]^2-\left[\frac{R}{\sqrt{\lambda}}\right]^2=1\quad or\quad X_0^2-R^2=\lambda^2>0\ .$$

This then produces

$$m(R\sinh\varphi+X_0\cosh\varphi)=m\sqrt{\lambda}\cosh(\varphi+\varphi_0)\ . \tag{3.13}$$

If $X_0<0$, then we can put $X_0=\sqrt{\lambda}\cosh\varphi_0$ and $R=\sqrt{\lambda}\sinh\varphi_0$ in order to obtain

$$m(R\sinh\varphi+X_0\cosh\varphi)=-m\sqrt{\lambda}\cosh(\varphi-\varphi_0)\ . \tag{3.14}$$

Combining Eqs. (3.12) and (3.13) we obtain

$$I_>=\int_{-\infty}^{\infty}d\varphi\, e^{im\sqrt{\lambda}\cosh(\varphi+\varphi_0)}=i\pi H_0^{(1)}(m\sqrt{\lambda})\ , \tag{3.15}$$

while combining Eqs. (3.12) and (3.14) produces

$$I_<=\int_{-\infty}^{\infty}d\varphi\, e^{-im\sqrt{\lambda}\cosh(\varphi-\varphi_0)}=-i\pi H_0^{(2)}(m\sqrt{\lambda})\ , \tag{3.16}$$

where $H_0^{(1)}$ and $H_0^{(2)}$ are Hankel's functions.

In view of Eq. (3.10), we have to write

$$I_1-I_2=i\pi[H_0^{(1)}(m\sqrt{\pi})+i\pi H_0^{(2)}(m\sqrt{\pi})]\ . \tag{3.17}$$

Using the fact that

$$J_0(m\sqrt{\lambda})=\tfrac{1}{2}[H_0^{(1)}(m\sqrt{\lambda})+H_0^{(2)}(m\sqrt{\lambda})]\ ,$$

we obtain

$$I_1-I_2=2i\pi J_0(m\sqrt{\pi})\ . \tag{3.18}$$

Combining Eqs. (3.10) and (3.17) we obtain

$$\text{Eq (3.9)}=\frac{(-1)}{8\pi}\frac{1}{R}\frac{\partial}{\partial R}J_0(m\sqrt{\lambda})\ . \tag{3.19}$$

Because,

$$\frac{\partial}{\partial R}J_0(m\sqrt{\lambda})=-J_1(m\sqrt{\lambda})m\frac{\partial}{\partial R}\sqrt{\lambda}=\frac{mR}{\sqrt{\lambda}}J_1(m\sqrt{\lambda})\ , \tag{3.20}$$

and, using the fact that

$$J_\nu(iz)=e^{i\nu\pi_1/2}I_\nu(z)\ , \tag{3.21}$$

we obtain (by making transformation from m to im)

$$\frac{G(R,N)}{mN}=\frac{(-1)}{8\pi}\frac{(mi)}{\sqrt{\lambda}}iI_1(m\sqrt{\lambda})=\frac{1}{8\pi}\frac{m}{\sqrt{\lambda}}I_1(m\sqrt{\lambda})\ , \qquad \lambda>0\ . \tag{3.22}$$

Taking into account Eqs. (3.1), (2.18), (2.19), and (3.8), we obtain the final result

$$G(\mathbf{R},N)=\frac{1}{2\pi N}\delta(\mathbf{R}^2-N^2)+\frac{Nm^2\theta(\lambda)}{8\pi\sqrt{\lambda}}I_1(m\sqrt{\lambda})\ . \tag{3.23}$$

Comparing this result with that given in Ref. [24] (e.g., see Sec. 16 of Ref. [24]), we find that our Eq. (3.23) is related to the Pauli-Jordan function via the transformation $m\to im$. Because in going from Eq. (3.9) to (3.10) we made a change from m to im, the result, Eq. (3.23), may or may not be correct. To check the correctness of this result we have to calculate the force $\mathbf{f}$ according to Eq. (2.5) and compare our results against those depicted in Fig. 1.

For $R<N$ employing Eqs. (2.5) and (3.22) and, in view of Eq. (3.3), we obtain after some algebra

$$N\mathbf{f}=\frac{y}{\sqrt{1-y^2}}\left[\frac{3}{4}\frac{N}{a}[I_2(x)+I_0(x)]\frac{1}{I_1(x)}-\frac{1}{\sqrt{1-y^2}}\right]\ , \tag{3.24}$$

where $y=\mathbf{R}/N$, $x=(3N/2a)\sqrt{1-y^2}$, and I_n, $n=0$–2, are the modified Bessel functions. The result given by Eq. (3.23) is plotted in Fig. 2. When compared against that of Fig. 1, it shows a complete equivalence and, therefore, justifies the correctness of our analytical continuation $m\to im$ and back.

IV. DISCUSSION

The results just obtained could serve as the reference for further development of the theory of randomly crosslinked networks of chains of arbitrary elasticity.

Although the elastic moduli of individual chains are of marginal importance in the network theory [8], it is nevertheless illuminating to compare the elastic moduli of fully flexible chains against that for chains of arbitrary stiffness. Based on the obtained results, we can formally define the elastic modulus ε of the individual chain according to the equation

$$\varepsilon=\frac{d\mathbf{f}}{d\langle\mathbf{R}\rangle}\ . \tag{4.1}$$

In the case of Gaussian chains, using Eq. (2.12), we obtain

$$\varepsilon=\frac{3}{Nl}\ , \tag{4.2}$$

while in the case of chains of arbitrary flexibility, using Eq. (3.23), we obtain after a little algebra,

$$\varepsilon N^2=\tfrac{1}{2}x[I_2(x)+I_0(x)]\frac{1}{I_1(x)}-1\ , \tag{4.3}$$

where $x=3N/2a$. To understand this result better, we notice that Eq. (4.2) can be rewritten as

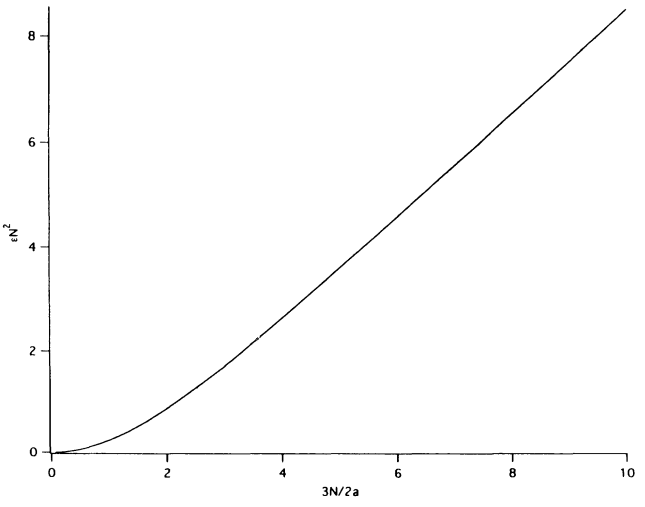

FIG. 3. Plot of elastic modulus εN^2 as a function of $x=3N/2a$ for polymer chains of arbitrary stiffness a.

$$\varepsilon N^2 = x \ , \tag{4.4}$$

where we have taken into account that $2a = l$ for $a \ll N$ [17]. If we use Eq. (4.4) for *arbitrary* a's, then for $x \gg 1$ noticing that $I_\nu(m) \alpha (\sqrt{2\pi m})^{-1} \exp(m)$ (for any ν's), we obtain from Eq. (4.3) the following asymptotic result:

$$\varepsilon N^2 \approx x - 1 \approx x \ , \tag{4.5}$$

which coincides with Eq. (4.4) as expected. In cases where x is of order unity (stiff chain limit), the results can be obtained numerically by using Eq. (4.3). The plot of εN^2 as function of x for arbitrary x is presented in Fig. 3. It indicates that the stiffness plays an appreciable role only for chains that are almost rigid. Otherwise, the elastic moduli ε for chains of arbitrary stiffness is practically the same as that for the fully flexible chains. It is very interesting to investigate if the same (or similar) result will hold for networks. This is left for future study. We also leave for further study the issue of the elastic response of semiflexible chains to the nematic environment [29]. To investigate this problem, we have to study the response of the Dirac chains to the nematic ordering field as was discussed in Sec. II. Finally, to study the arbitrary elongation of the polymer network would require us to use propagators defined on some Riemannian manifolds. This makes the network theory similar to that used in general relativity as was noticed some time ago by Sakharov [32] and developed by others [33].

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