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Statistical physics of the freely jointed chain

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Using the method of constraints proposed by S. F. Edwards and A. G. Goodyear [J. Phys. A **5**, 965 (1972); **5**, 1188 (1972)], we do a complete calculation of the canonical partition function of a freely jointed chain (FJC) from its classical Hamiltonian. We show how the constraints reduce the phase space of an ideal gas of monomers to the phase space of a FJC, and how they permit one to find the canonical partition function. By using this function, it is possible to study thermodynamical properties of FJC's and to build other thermodynamical ensembles via Laplace transforms. Thus we define a grand canonical ensemble where the monomer number of the FJC can fluctuate; in this ensemble, the FJC of infinite length is the asymptotic state at low and high temperatures. The critical exponents γ and ν for FJC's are calculated and found to be equal to the Gaussian polymer exponents. Connections between the properties of FJC's and random walks on regular lattices are also discussed. [S1063-651X(96)07106-1]

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I. INTRODUCTION

In the statistical theory of polymers, the first system which has been studied is the ideal polymer. When the degree of polymerization of the polymer is large, the polymer's end to end distance has a Gaussian distribution. This fact can be very well understood with the help of the central limit theorem [1]. The Gaussian model of a polymer is very useful because it retains important characteristics of the polymers, and allows one to interpret and calculate some of the critical exponents [2,3]. The values of these exponents can serve as a reference for more realistic models of polymers. This ideal model is thus used as a reference model for the study of macromolecules and polymers, in the same way as the ideal gas is used as a reference model for the study of real gases and liquids [2–6].

However, the description of an ideal polymer, based on a Gaussian distribution, or a random walk on a regular lattice, does not provide a direct relationship to the fundamental laws of statistical physics, especially the relationship between the Hamiltonian of the polymer and the canonical partition function. The present work aims at filling this gap.

To achieve this aim, we will use the simplest possible polymer model, the freely jointed chain (FJC), which we will also dub the ideal ghost polymer (IGP). This latter name seems to be a pleonasm in consideration of the customary use of the term ''ideal'' in polymer physics. In fact, in models of macromolecules and polymers, the interactions between monomers are taken to be (1) chemical and physical interactions (such as excluded volume effects, electrostatic interactions, etc.) and (2) geometrical constraints which define the structure and the geometry of the molecule.

The freely jointed chain has two major characteristics; it is a ghost polymer and an ideal polymer. By ''ghost,'' we then mean that there is interaction neither between the bonds nor between the monomers of the polymer. In this sense, the FJC is different from a polymer at its θ point [6], but some of the physical properties, independent of the ghost characteristic, will be common to both systems. For ideal we take the simplest possible geometrical constraints, namely, bonds with constant lengths. Thus a FJC is made up of $(N+1)$ massive points, linearly and freely jointed by N links of constant length (Fig. 1). This freely jointed chain was first studied by Kramers in 1946 [7], and since then by many others [8–12]. If we remove the constraints, we will have an ideal

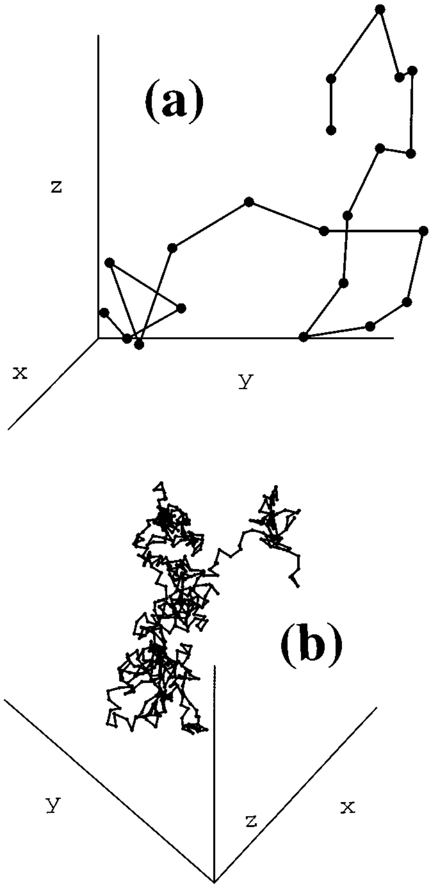

FIG. 1. Conformations of a freely jointed chain in three dimensions: (a) $N=20$; (b) $N=500$.

gas of $(N+1)$ distinguishable monomers. The geometrical constraints transform the system of $(N+1)$ distinguishable monomers into a macromolecule by changing the topology of the phase space associated with the $(N+1)$ monomers. The study of the thermodynamical and statistical properties of the macromolecule is equivalent to the study of an ideal gas in this modified phase space; this is the point of view adopted in the late 1960s by the Soviet school [6,13]. At the beginning of the 1970s, Edwards and Goodyear put forward a study of the dynamics of a polymer using the microcanonical ensemble and expressing the geometrical constraints with the help of Dirac distributions [9]. The main purpose of the present work is to compute the canonical partition function of the FJC and to study its equilibrium thermodynamical properties, especially the equilibrium states of a FJC which can exchange monomers with an infinite ideal gas of monomers.

The present work is organized as follows. In Sec. II, we study the reduction of phase space of a system of $(N+1)$ ideal and indistinguishable monomers under the action of the geometrical constraints expressed via Dirac distributions. The Dirac distributions allow us to express the partition function as an integral over the full phase space rather than over the reduced phase space which is topologically more complicated. In this way we will derive two nonintegrated analytical expressions for the partition function. In Sec. III, the temperature dependence of the partition function is extracted. We show that the partition function is the product of a function depending on the temperature and the degree of polymerization, for which a closed analytical expression is obtained, and a function depending only on the degree of polymerization. The latter is expressed as an integral involving Bessel functions. Sections IV and V are devoted to the study of this integral. In Sec. IV, we present an analytical study by series expansions of the exponentials appearing in the integral. These series expansions permit us to explore the analogy between quantum mechanics and polymer physics via Feynman formulation rather than via the Fokker-Planck equation [1,6,9]. Then, by using a method close to conventional renormalization theory and similar to the decimation method proposed by de Gennes [14,3,6], we give analytical approximations, involving hypergeometric functions, for the partition function of the FJC. In Sec. V, we perform a numerical study of the integral using a Monte Carlo algorithm together with an importance sampling method. Comparison of the numerical results with the analytical results of Sec. IV is made and an interpretation is given for the odd-even oscillation effect observed in polymers [15,16]: The agreement between the numerical and analytical results highlights the quality of the analytical approximations for the partition function of the FJC.

From the known canonical partition function of the FJC, we can derive its thermodynamical and statistical properties. In Sec. VI, we begin the study of these properties in the canonical ensemble for a system of FJC's. Then, considering the FJC as a gas of $(N+1)$ monomers, we can build the microcanonical and the grand canonical ensembles by Laplace transforms. In the grand canonical ensemble the low and high temperature states are FJC's of infinite length. This reentrant behavior is similar to the reentrant behavior of the less ordered phases observed in other systems, such as, for instance, in binary mixtures (for a review see [17]) or liquid crystals [18,19]. Finally, in order to compare the FJC model with other ideal polymer models, we compute the critical exponents γ and ν associated with the FJC. They are found to be equal to the critical exponents of the Gaussian polymer.

In this work, d is the dimension of the space containing the polymers. It is taken to be a real number greater than or equal to 2. Comparison with random walks on a regular lattice does not lead to any serious problems of interpretation as long as d has an integer value. When d takes noninteger values the random walks may be ill defined [20]. Recent work by Bender and co-workers [20,21] permits one, subject to topological regularity [22], to extend the model to noninteger dimensions of space.

II. REDUCTION OF THE PHASE SPACE BY CONSTRAINTS

Following Edwards and Goodyear [9], we express the geometrical constraints with Dirac distributions. These distributions reduce the phase space φ of an ideal gas of $(N+1)$ monomers to the restricted phase space φ_{rest} of the FJC. First, the monomers within the polymer have to become distinguishable. Nevertheless, in the polymer an indistinguishability remains due to the fact that one can label the monomers in one direction or the other. A memory effect is induced by the geometrical constraints imposed on the system. This effect may be interpreted as follows. At any point of the phase space φ_{rest}, the monomer numbered i remembers that its left and right neighbors are, e.g., the monomers $(i-1)$ and $(i+1)$, respectively. It is possible to reverse the labeling, so that the number of allowed permutations for the monomers in φ_{rest} is only 2!, whereas the number of allowed permutations in φ is $(N+1)!$ The memory effect results in a factor $(N+1)!/2!$ in the partition function. Thus it becomes impossible to distinguish the beginning of the polymer from its end. We will see that the Feynman rules associated with the polymer initiator and polymer terminator are the same.

To use Dirac distributions in the partition function without any dimensionality problem, we have to pay attention to their actions and meaning. The Dirac distributions are defined in such a way that for a physical observable A, there is the dimensional equation

$$\int d^nA\,\delta(A)=1\Rightarrow[\delta(A)]=[A]^{-n}. \tag{1}$$

So with the normalization (1) of the Dirac distribution, the probability distribution of the FJC in φ derived from that in the space φ_{rest} by expressing the geometrical constraint as a Dirac distribution must be multiplied by a constant having dimension such that in φ the distribution will be dimensionless [cf. Eq. (1)].

For the FJC, the constraints on the bonds are

$$\alpha\,\delta((\mathbf{r}_{i-1}-\mathbf{r}_i)^2-a^2), \tag{2}$$

where α is the multiplicative constant. Bonds with a constant length induce, from a dynamical point of view, a relation between the conjugate momenta associated with the degrees of freedom of the system [9]. This classical mechanics effect is one of the major difficulties encountered in simulations using the molecular dynamics method for the study of complex molecules when some degrees of freedom are frozen (see [23,24], and for a review [25]). In the FJC, the distribution (2) induces the dynamical constraint [9]

$$\gamma\delta((\mathbf{p}_{i-1}-\mathbf{p}_i)\cdot(\mathbf{r}_{i-1}-\mathbf{r}_i)), \tag{3}$$

where γ plays the same role as α.

The two constants γ and α must be related to physical parameters of the system. To do so, a convention concerning the canonical partition function must be chosen. A plausible choice, in view of the symmetry properties of the system, appears to be to take the partition function $Q_{\Diamond}^{(d)}(T,L)$ of a particle in a box of length L in a space of dimension d, equal to the partition function $Q_{\ominus}^{(d+1)}(T,L)$ of a particle moving on a hypersphere of radius L in a space of dimension $(d+1)$. $Q_{\Diamond}^{(d)}(T,L)$ is given by

$$\begin{aligned} Q_{\Diamond}^{(d)}(T,L) &= \frac{1}{h^d}\int_{\Diamond^{(d)}} d\mathbf{r}\, d\mathbf{p}\, \exp\left(-\frac{\beta}{2m}\mathbf{p}^2\right) \\ &= \left(\frac{mL^2}{2\pi\beta\hbar^2}\right)^{d/2}, \end{aligned} \tag{4}$$

and $Q_{\ominus}^{(d')}(T,L)$ is given by

$$Q_{\ominus}^{(d')}(T,L) = \frac{1}{h^{d'}}\int_{\ominus^{(d'-1)}} d\mathbf{r}\, d\mathbf{p}\, \exp\left(-\frac{\beta}{2m}\mathbf{p}^2\right). \tag{5}$$

With use of the Dirac distribution the latter can be written

$$\begin{aligned} Q_{\ominus}^{(d')}(T,L) = \frac{1}{h^{d'}}\,\alpha\gamma\int_{\Re^{d'}\times\Re^{d'}} d\mathbf{r}\, d\mathbf{p}\;\delta(\mathbf{r}^2-L^2)\,\delta(\mathbf{p}\cdot\mathbf{r}) \\ \times\exp\left(-\frac{\beta}{2m}\mathbf{p}^2\right). \end{aligned} \tag{6}$$

Use of the Fourier transform of the dynamical constraint,

$$\delta(\mathbf{p}\cdot\mathbf{r}) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\Omega\, \exp(j\Omega\mathbf{p}\cdot\mathbf{r}), \tag{7}$$

gives

$$Q_{\ominus}^{(d')}(T,L) = \frac{\alpha\gamma}{hL^2}\left(\frac{mL^2}{2\pi\beta\hbar^2}\right)^{(d'-1)/2}. \tag{8}$$

Thus, with $d'=d+1$, in order to have

$$Q_{\Diamond}^{(d)}(T,L) = Q_{\ominus}^{(d+1)}(T,L), \tag{9}$$

the equality $\alpha\gamma=hL^2$ is required. To satisfy the dimensional equation (1), dimensional analysis gives $\alpha=L^2$ and $\gamma=h$. Of course, by choosing another convention for the partition functions, for instance, by taking a hypersurface with a different geometry or by taking a different radius for the hypersphere, other relations could be obtained for the constants α and γ.

With the convention (9), the partition function of the FJC in the canonical ensemble is defined by the integral

$$Q_N^{(d)} = \frac{1}{2}\,\frac{1}{h^{(N+1)d}}\int_{\varphi_{\text{rest}}}\prod_{n=0}^{N} d\mathbf{r}_n d\mathbf{p}_n\, \exp\left(-\frac{\beta}{2m}\sum_{n=0}^{N}\mathbf{p}_n^2\right), \tag{10}$$

where the factor $\frac{1}{2}$ results from the indistinguishability effect discussed above. The topology of φ_{rest} may be complicated; in particular, it depends on the value of d. With the method of constraints, the domain of integration simplifies at the expense of a modification of the integrand. With the constants α and γ as determined above the partition function written in φ is

$$\begin{aligned} Q_N^{(d)} = \frac{1}{2}\,\frac{1}{h^{(N+1)d}}\,(ha^2)^N\int_{\varphi} d\mathbf{r}_0 d\mathbf{p}_0 \\ \times\prod_{n=1}^{N} d\mathbf{u}_n d\mathbf{p}_n\,\delta(\mathbf{u}_n^2-a^2)\,\delta((\mathbf{p}_n-\mathbf{p}_{n-1})\cdot\mathbf{u}_n) \\ \times\exp\left(-\frac{\beta}{2m}\sum_{n=0}^{N}\mathbf{p}_n^2\right), \end{aligned} \tag{11}$$

where the bond vectors are defined by

$$\mathbf{u}_n = \mathbf{r}_n - \mathbf{r}_{n-1} \quad \text{for } 1\leqslant n\leqslant N. \tag{12}$$

In the next section, we factorize the temperature dependence in the partition function (11).

III. DEPENDENCE ON TEMPERATURE OF THE PARTITION FUNCTION OF A FJC

To extract the dependence on temperature in the partition function of the FJC, the integration over all momenta must be done, and the variables chosen such that the nonintegrated part of the partition function depends only on N. As in Sec. II, the dynamical constraints are expressed through their Fourier transforms

$$\begin{aligned} \delta((\mathbf{p}_n-\mathbf{p}_{n-1})\cdot\mathbf{u}_n) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\Omega_n \\ \times\exp[j\Omega_n\mathbf{u}_n\cdot(\mathbf{p}_n-\mathbf{p}_{n-1})]. \end{aligned} \tag{13}$$

Using the property $\delta(\lambda x)=(1/|\lambda|)\delta(x)$ of the Dirac distribution and replacing (13) in (11), we obtain

$$\begin{aligned} Q_N^{(d)} = \frac{1}{h^{(N+1)d}}\,\frac{1}{2}\left(\frac{h}{2\pi}\right)^N\int d\mathbf{r}_0\prod_{n=1}^{N} d\mathbf{u}_n\,\delta\left(\frac{\mathbf{u}_n^2}{a^2}-1\right) \\ \times\int\prod_{n=1}^{N} d\Omega_n\int d\mathbf{p}_0\prod_{n=1}^{N} d\mathbf{p}_n\,\exp\left(-\frac{\beta}{2m}\sum_{n=0}^{N}\mathbf{p}_n^2\right. \\ \left.+j\sum_{n=1}^{N}\Omega_n\mathbf{u}_n\cdot(\mathbf{p}_n-\mathbf{p}_{n-1})\right). \end{aligned} \tag{14}$$

The integral over $\mathbf{p}_n$ is a Gaussian integral,

$$\int dX\,\exp(-\tfrac{1}{2}X^tAX+J^tX) = \left[\det\left(\frac{A}{2\pi}\right)\right]^{-1/2}\exp(\tfrac{1}{2}J^tA^{-1}J), \tag{15}$$

where

$$X=(\mathbf{p}_n)_{0\leqslant n\leqslant N},$$

$$J=j[-\Omega_1\mathbf{u}_1,\{(\Omega_n\mathbf{u}_n-\Omega_{n+1}\mathbf{u}_{n+1})\},\Omega_N\mathbf{u}_N], \tag{16}$$

$$A=(\beta/m)(I_{(N+1)}\otimes I_d),$$

$$\left[\det\left(\frac{A}{2\pi}\right)\right]^{-1/2}=\left(\frac{2\pi m}{\beta}\right)^{d(N+1)/2}, \tag{17}$$

and

$$\tfrac{1}{2}J^tA^{-1}J=-\frac{m}{\beta}\left(\sum_{n=1}^{N}\Omega_n^2\mathbf{u}_n^2-\sum_{n=1}^{N-1}(\Omega_n\mathbf{u}_n)\cdot(\Omega_{n+1}\mathbf{u}_{n+1})\right). \tag{18}$$

To integrate over $\mathbf{r}_0$, the box which contains the polymer is assumed to be larger than the typical size of the polymer. After integration over all the momenta and over $\mathbf{r}_0$ Eq. (14) becomes

$$Q_N^{(d)}=\frac{1}{2}\,\frac{1}{h^{(N+1)d}}\left(\frac{h}{2\pi}\right)^N V\left(\frac{2\pi m}{\beta}\right)^{d(N+1)/2}\times\int\prod_{n=1}^{N}d\mathbf{u}_n\,\delta\!\left(\frac{\mathbf{u}_n^2}{a^2}-1\right)\int\prod_{n=1}^{N}d\Omega_n\times\exp\left[-\frac{m}{\beta}\left(\sum_{n=1}^{N}\Omega_n^2\mathbf{u}_n^2-\sum_{n=1}^{N-1}(\Omega_n\mathbf{u}_n)\cdot(\Omega_{n+1}\mathbf{u}_{n+1})\right)\right]. \tag{19}$$

The definition

$$\hat{\mathbf{u}}_n=\frac{1}{a}\,\mathbf{u}_n \tag{20}$$

allows us to work with dimensionless bond vectors.

The integrand in (19) is always positive; permutation of the order of integrations and use of the property $\int f(x)g(x)\delta(x)dx=f(0)\int g(x)\delta(x)dx$ gives

$$Q_N^{(d)}=\frac{1}{2}\,\frac{1}{h^{(N+1)d}}\left(\frac{h}{2\pi}\right)^N Va^{Nd}\left(\frac{2\pi m}{\beta}\right)^{d(N+1)/2}\times\int\prod_{n=1}^{N}d\Omega_n\exp\left(-\frac{ma^2}{\beta}\sum_{n=1}^{N}\Omega_n^2\right)\times\int\prod_{n=1}^{N}d\hat{\mathbf{u}}_n\,\delta(\hat{\mathbf{u}}_n^2-1)\times\exp\left[\frac{ma^2}{\beta}\left(\sum_{n=1}^{N-1}(\Omega_n\hat{\mathbf{u}}_n)\cdot(\Omega_{n+1}\hat{\mathbf{u}}_{n+1})\right)\right]. \tag{21}$$

The last equation shows how the dynamical constraints induce a coupling between the bond vectors. The integration over the set of variables $\{\hat{\mathbf{u}}_n\}$ is not straightforward.

Defining

$$U^{(d)}=\int\prod_{n=1}^{N}d\hat{\mathbf{u}}_n\,\delta(\hat{\mathbf{u}}_n^2-1)\times\exp\left[\frac{ma^2}{\beta}\left(\sum_{n=1}^{N-1}(\Omega_n\hat{\mathbf{u}}_n)\cdot(\Omega_{n+1}\hat{\mathbf{u}}_{n+1})\right)\right] \tag{22}$$

and $x=(ma^2/\beta)\Omega_{N-1}\Omega_N$, the integral over $\hat{\mathbf{u}}_N$ is

$$z^{(d)}(x)=\int d\hat{\mathbf{u}}_N\,\delta(\hat{\mathbf{u}}_N^2-1)\exp(x\hat{\mathbf{u}}_{N-1}\cdot\hat{\mathbf{u}}_N), \tag{23}$$

$$z^{(d)}(x)=\frac{x}{2\pi j}\int d\hat{\mathbf{u}}_N\int_{-j\infty}^{+j\infty}du\,\exp[xu(1-\hat{\mathbf{u}}_N^2)]\times\exp(x\hat{\mathbf{u}}_{N-1}\cdot\hat{\mathbf{u}}_N), \tag{24}$$

$$z^{(d)}(x)=\frac{x}{2\pi j}\int_{\alpha-j\infty}^{\alpha+j\infty}dr\,\exp(xr)\int d\hat{\mathbf{u}}_N\times\exp[-x(r\hat{\mathbf{u}}_N^2-\hat{\mathbf{u}}_{N-1}\cdot\hat{\mathbf{u}}_N)]. \tag{25}$$

In Eqs. (23)–(25), the Dirac distribution has been expressed through its Fourier transform, the order of integrations has been permuted, and we have set $r=u+\alpha$ with α such that $(u+\alpha)\hat{\mathbf{u}}_N^2-\hat{\mathbf{u}}_{N-1}\cdot\hat{\mathbf{u}}_N>0$.

The integral over $\hat{\mathbf{u}}_N$ is Gaussian, with the result

$$z^{(d)}(x)=\frac{x}{2\pi j}\int_{\alpha-j\infty}^{\alpha+j\infty}dr\left(\frac{\pi}{xr}\right)^{d/2}\exp\left[x\left(r+\frac{1}{4r}\right)\right], \tag{26}$$

$$z^{(d)}(x)=\frac{1}{2}\,\frac{x}{2\pi j}\left(\frac{2\pi}{x}\right)^{d/2}\int_{2\alpha-j\infty}^{2\alpha+j\infty}dw(w)^{-d/2}\times\exp\left[\frac{x}{2}\left(w+\frac{1}{w}\right)\right], \tag{27}$$

$$z^{(d)}(x)=\frac{1}{2}\,x\left(\frac{2\pi}{x}\right)^{d/2}I_{(d/2-1)}(x). \tag{28}$$

The function $I_\mu(x)$ is the modified Bessel function of the first kind. The integral $z^{(d)}(x)$ is independent of the direction of $\hat{\mathbf{u}}_{N-1}$, but depends on Ω_{N-1} and Ω_N. The integrals over each bond are independent and the integral over the bond $\hat{\mathbf{u}}_1$ produces a factor $S_d(1)$, the surface of a sphere with a unit radius in a space of d dimensions. The dependence on Ω_1 is included in the integral over the bond $\hat{\mathbf{u}}_2$. Equation (22) can be written in the form

$$U^{(d)}=S_d(1)\left(\frac{ma^2}{2\beta}\right)^{(N-1)}\times\left(\frac{2\pi\beta}{ma^2}\right)^{d(N-1)/2}\prod_{n=1}^{(N-1)}(\Omega_n\Omega_{n+1})^{(1-d/2)}\times I_{(d/2-1)}\left(\frac{ma^2}{\beta}\Omega_n\Omega_{n+1}\right). \tag{29}$$

A particular case of this result has been obtained by Stanley [26] for a chain of classical isotropic spins with nearest neighbor interactions. Stanley's result is recovered if all Ω_n's are taken to be equal. In this case $U^{(d)}$ is proportional to the partition function obtained by Stanley. If some other sets of $\{\Omega_n\}$ values are chosen, partition functions of different spin systems can be obtained; for instance, if we set $\Omega_n=\Omega$ for $n\neq i$ and $\Omega_i\neq\Omega$, the partition function of a classical isotropic spin chain with an impurity spin on the site i is obtained. In spin systems, the coupling between spins results from the magnetic field induced by the spins. In the FJC, the coupling between bond vectors results from the dynamical constraints induced by the bonds.

Use of the transformed variables

$$\gamma_n=\left(\frac{ma^2}{\beta}\right)^{1/2}\Omega_n, \tag{30}$$

leads to an integral which depends on N only. After straightforward simplifications, the partition function (21) becomes

$$Q_N^{(d)}=S_d(1)V\left(\frac{m}{4\pi^2\beta\hbar^2}\right)^{d/2}\left[\left(\frac{1}{2}\right)^{2/(d-1)}\frac{ma^2}{\beta\hbar^2}\right]^{N(d-1)/2}J_N^{(d)}, \tag{31}$$

where $\hbar=h/2\pi$ and

$$J_N^{(d)}=\int\prod_{n=1}^{N}d\gamma_n\left(\prod_{n=1}^{(N-1)}(\gamma_n\gamma_{n+1})^{(1-d/2)}\times I_{(d/2-1)}(\gamma_n\gamma_{n+1})\right)\exp\left(-\sum_{n=1}^{N}\gamma_n^2\right). \tag{32}$$

All the temperature dependence is explicitly contained in (31), whereas the integral (32) contains all the nontrivial dependence on N. The main difficulty in computing the latter integral comes from the coupling between γ_n and γ_{n+1}.

For the transformation

$$\omega_n=\gamma_{n-1}\gamma_n\quad\text{for }2\leqslant n\leqslant N,\qquad \omega_1=\gamma_1, \tag{33}$$

the Jacobian matrix is triangular, giving the Jacobian

$$\det[Ja(\omega_i)]=\prod_{n=2}^{N}\prod_{p=1}^{n-1}(\omega_{(n-p)})^{(-1)^p}. \tag{34}$$

Using this transformation in (32), the nonintegrated part becomes

$$J_N^{(d)}=\int\prod_{n=1}^{N}d\omega_n|\det[Ja(w)]|\left(\prod_{n=2}^{N}(\omega_n)^{(1-d/2)}\times I_{(d/2-1)}(\omega_n)\right)\exp\left(-\sum_{n=2}^{N}\prod_{p=1}^{n-1}(\omega_{(n-p)}^2)^{(-1)^p}\omega_n^2-\omega_1^2\right). \tag{35}$$

In order to identify the contribution to $Q_N^{(d)}$ from each bond, we set

$$A_N=\left|\prod_{p=1}^{N-1}(\omega_{(N-p)})^{(-1)^p}\right| \tag{36}$$

and

$$f_N^{(d)}=A_N\int d\omega_N\omega_N^{(1-d/2)}I_{(d/2-1)}(\omega_N)\times\exp\left(-\prod_{p=1}^{N-1}(\omega_{(N-p)}^2)^{(-1)^p}\omega_N^2\right). \tag{37}$$

For the Bessel function, we use the representation

$$I_\mu(x)=\frac{(x/2)^\mu}{\Gamma(\mu+1/2)\Gamma(1/2)}\int_{-1}^{1}(1-t^2)^{(\mu-1/2)}e^{xt}dt. \tag{38}$$

IV. ANALYTICAL STUDY OF $J_N^{(d)}$

In this section, devoted to the degree of polymerization, we try to compute the function $J_N^{(d)}$ for all values of N. The computation is made by extracting the contribution of each bond to $J_N^{(d)}$.

By series expansion of the exponentials, each integral is transformed into a sum over the natural numbers. There are $(N-1)$ sums of that kind for a FJC with N bonds. These sums show that $J_N^{(d)}$ can be expressed in terms of a special function having the special value $\frac{1}{4}$ for its arguments. If one were able to find an analytical form for this function, then one would have found an analytical form for the partition function of a FJC. Unfortunately, this function is directly related to the multiple hypergeometric functions, so that an analytical form of the partition function of a FJC can easily be obtained only for small values of N. On the other hand, the series expansion of $J_N^{(d)}$ is useful to exhibit the analogy between polymer physics and quantum mechanics via the Feynman formulation. Usually, this analogy is demonstrated by using the Fokker-Planck equation for the probability distribution function of the end to end distance [1,6,9,27]; it may also be described via Green's functions [6]. This analogy enables the use of methods closely related to the conventional renormalization of the full propagator [28] to derive various approximations for $J_N^{(d)}$.

To test the analytical approximations derived in this section a Monte Carlo algorithm described in the next section is used to obtain numerical results for $J_N^{(d)}$. The agreement between the approximate analytical results of this section and the numerical results of the next section will show the reliability of the theoretical approach.

The present section is divided into five subsections. In Sec. IV A, we make the series expansion of $J_N^{(d)}$. In Sec. IV B, we define the function related to $J_N^{(d)}$. This function can be defined in several ways depending on the number of variables the special value $\frac{1}{4}$ is assigned to. The series expansion of $J_N^{(d)}$ is composed of $(N-1)$ sums; thus the function giving $J_N^{(d)}$ will be a scalar field on a Euclidean space of dimension $(N-1)$. In Sec. IV C, we write the Feynman rules for the computation of $J_N^{(d)}$. In Sec. IV D, we use these Feynman rules to develop the conventional renormalization and derive approximations. Finally, in Sec. IV E, we compute $J_N^{(d)}$ exactly for small values of N.

A. Series expansion of $J_N^{(d)}$

In the relation (37) defining $f_N^{(d)}$, the Bessel functions are expressed with their representation (38); this gives

$$f_N^{(d)}=\frac{(1/2)^{(d/2-1)}}{\Gamma([d-1]/2)\Gamma(1/2)}A_N\int_{-\infty}^{+\infty}d\omega_N \times\int_{-1}^{1}(1-t_{N-1}^2)^{(d-3)/2}e^{-A_N^2\omega_N^2+\omega_N t_{N-1}}dt_{N-1}. \tag{39}$$

Since in (39) the integrand is always positive and the value of $f_N^{(d)}$ finite, the integration orders can be permutated. The integral over ω_N is Gaussian; thus

$$f_N^{(d)}=\frac{(1/2)^{d/2}}{\Gamma([d-1]/2)}\int_0^1 dt_{N-1}(1-t_{N-1}^2)^{(d-3)/2}e^{-t_{N-1}^2/4A_N^2}. \tag{40}$$

The factor A_N defined in (36) and stemming from the Jacobian (34) is exactly cancelled by a factor $\sqrt{A_N^2}=|A_N|=A_N$ coming from the Gaussian integration. Starting from (40), we may either put (40) into (35) to extract $f_{N-1}^{(d)}$ and make the Gaussian integration over ω_{N-1}, or make a series expansion of the exponential of (40) and integrate over t_{N-1}. In this section the latter way is chosen, while the former will be used in the next section. Since the integral is convergent both ways must lead to the same result. From the definition of A_N (36), the following relation holds:

$$\frac{1}{A_N^2}=A_{N-1}^2\omega_{N-1}^2. \tag{41}$$

The series expansion of the exponential gives

$$f_N^{(d)}=\frac{(1/2)^{d/2}}{\Gamma([d-1]/2)}\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{4}\right)^n\left(\frac{1}{A_N^2}\right)^n \times\int_0^1 dt_N(1-t_N^2)^{(d-3)/2}t_N^{2n}, \tag{42}$$

which, after a straightforward integration, leads to

$$f_N^{(d)}=\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)^{d/2}\sum_{n=0}^{\infty}\frac{1}{n!}\frac{\Gamma(n+1/2)}{\Gamma(n+d/2)}\left(\frac{1}{4}\right)^n A_{N-1}^{2n}\omega_{N-1}^{2n}. \tag{43}$$

Substituting (43) into (35), $f_{N-1}^{(d)}$ is extracted as

$$f_{N-1}^{(d)}=\left(\frac{1}{2}\right)^{d/2}\frac{1}{2}\sum_{n=0}^{\infty}\frac{1}{n!}\frac{\Gamma(n+1/2)}{\Gamma(n+d/2)}\left(\frac{1}{4}\right)^n A_{N-1}^{2n}A_{N-1} \times\frac{(1/2)^{(d/2-1)}}{\Gamma([d-1]/2)\Gamma(1/2)}\int_{-1}^{1}dt_{N-1}(1-t_{N-1}^2)^{(d-3)/2} \times\int_{-\infty}^{+\infty}d\omega_{N-1}\omega_{N-1}^{2n}\exp(-A_{N-1}^2\omega_{N-1}^2 +t_{N-1}\omega_{N-1}), \tag{44}$$

and becomes, after integration over ω_{N-1},

$$f_{N-1}^{(d)}=\frac{1}{2}\left(\frac{1}{2}\right)^{d/2}\sum_{n_1=0}^{\infty}\frac{1}{n_1!}\frac{\Gamma(n_1+1/2)}{\Gamma(n_1+d/2)}\left(\frac{1}{4}\right)^{n_1}A_{N-1}^{2n_1} \times\int_{-1}^{1}dt_{N-1}(1-t_{N-1}^2)^{(d-3)/2} \times\frac{1}{A_{N-1}^2}\frac{d^{2n_1-1}}{dt_{N-1}^{2n_1-1}}\left[t_{N-1}\exp\left(\frac{t_{N-1}^2}{4A_{N-1}^2}\right)\right]. \tag{45}$$

Expanding the exponential in (45), taking the derivative, and integrating gives

$$f_{N-1}^{(d)}=\left(\frac{1}{2}\right)^{d/2}\left(\frac{1}{2}\right)^{d/2}\sum_{n_1=0}^{\infty}\frac{1}{n_1!}\frac{\Gamma(n_1+1/2)}{\Gamma(n_1+d/2)} \times\left(\frac{1}{4}\right)^{n_1}\left(\frac{1}{4}\right)^{n_1}\frac{1}{2}\sum_{n_2=0}^{\infty}\frac{1}{(n_2+n_1-1)!} \times\frac{[2(n_2+n_1)-1]!}{(2n_2)!}\left(\frac{1}{4}\right)^{n_2}\frac{\Gamma(n_2+1/2)}{\Gamma(n_2+d/2)}\left(\frac{1}{A_{N-1}}\right)^{2n_2}. \tag{46}$$

From the relation

$$(2n)!=\frac{2^{2n}}{\sqrt{\pi}}n!\Gamma(n+\tfrac{1}{2}), \tag{47}$$

it follows that

$$\frac{[2(n_2+n_1)-1]!}{(n_2+n_1-1)!(2n_2)!}=\frac{4^{n_1}}{2}\,\frac{1}{(n_2)!}\,\frac{\Gamma(n_2+n_1+1/2)}{\Gamma(n_2+1/2)} \tag{48}$$

and so with use of relation (41) the second sum is found to be

$$f_{N-1}^{(d)}=\left(\frac{1}{2}\right)^{d/2}\frac{1}{2}\sum_{n_1=0}^{\infty}\frac{1}{n_1!}\,\frac{\Gamma(n_1+1/2)}{\Gamma(n_1+d/2)}\left(\frac{1}{4}\right)^{n_1}\left(\frac{1}{2}\right)^{d/2}\times\left(\frac{1}{2}\right)\sum_{n_2=0}^{\infty}\frac{1}{n_2!}\,\frac{\Gamma(n_1+n_2+1/2)}{\Gamma(n_2+d/2)}\left(\frac{1}{4}\right)^{n_2}A_{N-2}^{2n_2}\omega_{N-2}^{2n_2}. \tag{49}$$

The method is repeated until $N-p=2$; thus

$$f_2^{(d)}=\left(\frac{1}{2}\right)^{d(N-1)/2}\left(\frac{1}{2}\right)^{(N-1)}\sum_{n_1=0}^{\infty}\frac{1}{n_1!}\,\frac{\Gamma(n_1+1/2)}{\Gamma(n_1+d/2)}\left(\frac{1}{4}\right)^{n_1}\sum_{n_2=0}^{\infty}\frac{1}{n_2!}\,\frac{\Gamma(n_1+n_2+1/2)}{\Gamma(n_2+d/2)}\left(\frac{1}{4}\right)^{n_2}\cdots$$
$$\times\sum_{n_p=0}^{\infty}\frac{1}{n_p!}\,\frac{\Gamma(n_{p-1}+n_p+1/2)}{\Gamma(n_p+d/2)}\left(\frac{1}{4}\right)^{n_p}\cdots\sum_{n_{N-2}=0}^{\infty}\frac{1}{n_{N-2}!}\,\frac{\Gamma(n_{N-3}+n_{N-2}+1/2)}{\Gamma(n_{N-2}+d/2)}\left(\frac{1}{4}\right)^{n_{N-2}}\sum_{n_{N-1}=0}^{\infty}\frac{1}{n_{N-1}!}$$
$$\times\frac{\Gamma(n_{N-2}+n_{N-1}+1/2)}{\Gamma(n_{N-1}+d/2)}\left(\frac{1}{4}\right)^{n_{N-1}}A_1^{2n_{N-1}}\omega_1^{2n_{N-1}}. \tag{50}$$

Finally, by definition of $f_1^{(d)}$ and $J_N^{(d)}$,

$$J_N^{(d)}=f_1^{(d)}=\int_{-\infty}^{+\infty}d\omega_1 f_2^{(d)}\,\exp(-\omega_1^2), \tag{51}$$

with $\int_{-\infty}^{+\infty}d\omega_1\omega_1^{2n_{N-1}}\,\exp(-\omega_1^2)=\Gamma(n_{N-1}+\frac{1}{2})$, which closes the expansion. Thus the series expansion of $J_N^{(d)}$ is

$$J_N^{(d)}=\left(\frac{1}{2}\right)^{(N-1)}\left(\frac{1}{2}\right)^{d(N-1)/2}\sum_{n_1=0}^{\infty}\frac{1}{n_1!}\,\frac{\Gamma(n_1+1/2)}{\Gamma(n_1+d/2)}\left(\frac{1}{4}\right)^{n_1}\sum_{n_2=0}^{\infty}\frac{1}{n_2!}\,\frac{\Gamma(n_1+n_2+1/2)}{\Gamma(n_2+d/2)}\left(\frac{1}{4}\right)^{n_2}\cdots\sum_{n_p=0}^{\infty}\frac{1}{n_p!}\,\frac{\Gamma(n_{p-1}+n_p+1/2)}{\Gamma(n_p+d/2)}$$
$$\times\left(\frac{1}{4}\right)^{n_p}\cdots\sum_{n_{N-2}=0}^{\infty}\frac{1}{n_{N-2}!}\,\frac{\Gamma(n_{N-3}+n_{N-2}+1/2)}{\Gamma(n_{N-2}+d/2)}\left(\frac{1}{4}\right)^{n_{N-2}}\sum_{n_{N-1}=0}^{\infty}\frac{1}{n_{N-1}!}\,\frac{\Gamma(n_{N-2}+n_{N-1}+1/2)}{\Gamma(n_{N-1}+d/2)}$$
$$\times\Gamma\left(n_{N-1}+\frac{1}{2}\right)\left(\frac{1}{4}\right)^{n_{N-1}}. \tag{52}$$

(This relation can be seen as a propagation over a chain of integer number.) The relation (52) is far from simple, but has the advantage of showing that $J_N^{(d)}$ is given by the particular value $\frac{1}{4}$ of a special function that we shall call $g_N^{(d)}(x)$. The series expansion of this function is obtained from (52) by replacing $\frac{1}{4}$ by x, imposing the constraint $n=\Sigma_{i=1}^{(N-1)}n_i$ on the n_i, and extending the sum over n from 0 to ∞. In each sum, the factor $\frac{1}{4}$ can be associated with an independent variable x_i, the ith component of a vector $\mathbf{x}$ in the Euclidean space of dimension $(N-1)$. $g_N^{(d)}(\mathbf{x})$ is, with this definition, a scalar field. We will use this latter definition of $g_N^{(d)}$ which is easier to manipulate, rather than the functional definition where there is a constraint $n=\Sigma_{i=1}^{(N-1)}n_i$.

B. The scalar field $g_N^{(d)}$

The field $g_N^{(d)}$ can be expressed in terms of hypergeometric functions. The following definitions will be used (see [29]):

$${}_2F_1(a,b;c;x)=\sum_{n=0}^{\infty}\frac{1}{n!}\,\frac{(n,a)(n,b)}{(n,c)}\,x^n, \tag{53}$$

for the hypergeometric function and

$${}_1F_1(a;c;x)=\sum_{n=0}^{\infty}\frac{1}{n!}\,\frac{(n,a)}{(n,c)}\,x^n, \tag{54}$$

for the degenerate hypergeometric function;

$$(n,a)=\frac{\Gamma(n+a)}{\Gamma(a)} \tag{55}$$

is the Pochhammer symbol [29], and

$$g_N^{(d)}(0)=\left(\frac{1}{2}\right)^{(N-1)}\left(\frac{1}{2}\right)^{d(N-1)/2}\Gamma\left(\frac{1}{2}\right)\left(\frac{\Gamma(1/2)}{\Gamma(d/2)}\right)^{(N-1)}. \tag{56}$$

In each sum over the integer n_i, the factors $(\frac{1}{4})^{n_i}$ are changed into $x_i^{n_i}$ where x_i is the ith component of a vector $\mathbf{x}$ of a Euclidean space of dimension $(N-1)$. With the previous definitions, the series expansion of $J_N^{(d)}$ leads to the multiple series expansion of $g_N^{(d)}(\mathbf{x})$ according to

$$g_N^{(d)}(\mathbf{x})=g_N^{(d)}(\mathbf{0})\sum_{n_1=0}^{\infty}\frac{1}{n!}\,\frac{(n_1,1/2)}{(n_1,d/2)}\,(x_1)^{n_1}\sum_{n_2=0}^{\infty}\frac{1}{n_2!}\,\frac{(n_1+n_2,1/2)}{(n_2,d/2)}\,(x_2)^{n_2}\cdots\sum_{n_p=0}^{\infty}\frac{1}{n_p!}\,\frac{(n_{p-1}+n_p,1/2)}{(n_p,d/2)}\,(x_p)^{n_p}\cdots$$
$$\times\sum_{n_{N-2}=0}^{\infty}\frac{1}{n_{N-2}!}\,\frac{(n_{N-3}+n_{N-2},1/2)}{(n_{N-2},d/2)}\,(x_{(N-2)})^{n_{N-2}}\sum_{n_{N-1}=0}^{\infty}\frac{1}{n_{N-1}!}\,\frac{(n_{N-2}+n_{N-1},1/2)}{(n_{N-1},d/2)}\left(n_{N-1},\,\frac{1}{2}\right)(x_{(N-1)})^{n_{N-1}}. \tag{57}$$

Derivatives of all orders at the origin of the scalar field are thus known. They can be expressed with the help of the derivatives of the hypergeometric functions. For example, the gradiant of $g_N^{(d)}$ at the origin is

$$[\boldsymbol{\nabla} g_N^{(d)}(\mathbf{x})]_{\mathbf{0}}=g_N^{(d)}(\mathbf{0})\begin{bmatrix}\partial_{x_1} & {}_1F_1(1/2;d/2;0)\\ \vdots & \vdots\\ \partial_{x_{N-2}} & {}_1F_1(1/2;d/2;0)\\ \partial_{x_{N-1}} & {}_2F_1(1/2,1/2;d/2;0)\end{bmatrix}, \tag{58}$$

and derivatives of all orders in the direction of each axis of the Euclidean space at the origin are given by

$$\partial_{x_i}^{n_i} g_N^{(d)}(\mathbf{x})|_{\mathbf{x}=\mathbf{0}}=g_N^{(d)}(\mathbf{0})\partial_{x_i}^{n_i}\;{}_1F_1(1/2;d/2;0)$$
$$\text{for}\quad 1\leqslant i\leqslant N-2,$$
$$\partial_{x_{N-1}}^{n_{N-1}} g_N^{(d)}(\mathbf{x})|_{\mathbf{x}=\mathbf{0}}=g_N^{(d)}(\mathbf{0})\partial_{x_{N-1}}^{n_{N-1}}\;{}_2F_1(1/2,1/2;d/2;0)$$
$$\text{for}\quad N-1. \tag{59}$$

One can note that the value of the field $g_N^{(d)}$ along each axis of the Euclidean space is known, since, for $|x_i|<1$,

$$g_N^{(d)}(x_i\mathbf{e}_i)=g_N^{(d)}(\mathbf{0})\;{}_1F_1(1/2;d/2;x_i)\quad\text{for}\quad 1\leqslant i\leqslant N-2,$$
$$g_N^{(d)}(x_{N-1}\mathbf{e}_{N-1})=g_N^{(d)}(\mathbf{0})\;{}_2F_1(1/2,1/2;d/2;x_{N-1})$$
$$\text{for}\quad N-1. \tag{60}$$

C. Feynman rules for $J_N^{(d)}$

Equation (52) can be interpreted as a sum over all allowed propagations on an integer linear chain. The chain is made of $(N-1)$ sites; with each site a multiplicity n_i and a weight $(1/n_i!)[1/(n_i,d/2)](x_i)^{n_i}$ are associated. On site 1, a propagation is initialized with a multiplicity n_1 by a polymer initiator $(n_1,\frac{1}{2})$. This perturbation of the integer chain propagates itself to site 2 with a propagator $(n_1+n_2,\frac{1}{2})$, from site 2 to site 3 in the same way, and so on until the perturbation reaches a polymer terminator on site $(N-1)$ of the same form as the polymer initiator $(n_{N-1},\frac{1}{2})$. The sum over all the allowed propagations gives the behavior in N of the partition function of the FJC. This is, of course, closely related to the decomposition with Green's functions [6,30]. The Feynman rules associated with this propagation are, for the sites,

$$\bigcirc_p\equiv\frac{1}{p!}\,\frac{1}{(p,d/2)}\,(x)^p, \tag{61}$$

and for the propagators,

$${}_n\!\!-\!\!\!-_p\equiv(n+p,\tfrac{1}{2})=(p+n,\tfrac{1}{2}) \tag{62}$$

(one can observe that the propagators are not oriented). For the polymer initiator and the polymer terminator the rules are the same:

$$\bullet_n\equiv(n,\tfrac{1}{2})\bigcirc_n. \tag{63}$$

The rules (62) and (63) preserve the symmetry by inversion of the labeling in the partition function. With the Feynman rules Eq. (57) becomes

$$g_N^{(d)}(\mathbf{x})=g_N^{(d)}(\mathbf{0})\sum_{n_1}^{\infty}\cdots\sum_{n_p}^{\infty}\cdots\sum_{n_{N-1}}^{\infty}(\bullet_{n_1}\!-\!\!\!-\bigcirc_{n_2}\!-\!\!\!-\bigcirc_{n_3}\cdots\bigcirc_{n_{p-1}}\!-\!\!\!-\bigcirc_{n_p}\cdots\bigcirc_{n_{N-2}}\!-\!\!\!-\bullet_{n_{N-1}}). \tag{64}$$

The memory effect appears explicitly in the last equation. If one considers that each site is associated with an event and the numbering of the sites with a discrete time, then the system will keep memory of the relative chronology of events but not of the direction of time.

D. Calculations with Feynman rules

From the definitions (53) and (54), it is straightforward that the relations

$$\sum_{n_2=0}^{\infty}(\bigcirc_{n_1}\!-\!\!\!-\bigcirc_{n_2}\!-\!\!\!-\bigcirc_{n_3})=\bigcirc_{n_1}\!=\!\!\!=\bigcirc_{n_3}, \tag{65}$$

$$\sum_{n_2=0}^{\infty}(\bullet_{n_1}\!-\!\circ_{n_2}\!-\!\circ_{n_3})=\bullet_{n_1}\!=\!\circ_{n_3} \tag{66}$$

hold, where the double propagator is defined as

$$_{n_{-1}}\!=\!_{n_{i+1}}\equiv {}_2F_1\left(\frac{1}{2}+n_{i-1},\ \frac{1}{2}+n_{i+1};\ \frac{d}{2};x_i\right). \tag{67}$$

As in particle physics, the last equation is the full propagator of a scalar field to first order in λ, when the interaction is a composite operator like $\frac{1}{2}\lambda\Phi^2$ [28].

If N is odd, taking $(N-1)=2P$, Eq. (64) becomes

$$g_{2P+1}^{(d)}(\mathbf{x})=g_{2P+1}^{(d)}(\mathbf{0})\sum_{n_1,\ldots,n_{(2P-1)},n_{2P}=0}^{\infty}(\bullet_{n_1}\!=\!\circ_{n_3}\!=\!\circ_{n_5}\cdots\circ_{n_{(2P-3)}}\!=\!\circ_{n_{(2P-1)}}\!-\!\bullet_{n_{2P}}). \tag{68}$$

On the contrary, if N is even, taking $N-1=2P-1$, Eq. (64) becomes

$$g_{2P}^{(d)}(\mathbf{x})=g_{2P}^{(d)}(\mathbf{0})\sum_{n_1,\ldots,n_{2P-1}=0}^{\infty}(\bullet_{n_1}\!=\!\circ_{n_3}\!=\!\circ_{n_5}\cdots\circ_{n_{(2P-5)}}\!=\!\circ_{n_{(2P-3)}}\!=\!\bullet_{n_{(2P-1)}}). \tag{69}$$

Equations (68) and (69) show that there is a nontrivial parity effect in the partition function of the FJC; the single propagator in (68) may be placed anywhere in the integer chain. This odd-even effect manifests itself by oscillations in some functions derived from the partition function. It has been observed by Fisher and Hiley [15] in a counting of self-avoiding walks (SAW's) and recently by Grassberger and Hegger [16] in simulations of Θ polymers in two and three dimensions.

It is difficult to contract the double propagators (67) as is done for the single propagators, because of other odd-even effects of higher order that appear and because of the need for multiple hypergeometric functions. On the other hand, the double propagators can be developed in single propagators (stage *b*), and the single propagators transformed into double propagators (stage *a*). This manipulation repeated with the rules (65) and (66) generates a kind of self-similar fractal sequence. In Fig. 2, the first three generations of this fractalization are shown for a fractal initiator given by $N=3$. There are holes in the prefractal sequence relative to the sequence $g_{2P}^{(d)}(\mathbf{x})$. If the fractal initiator is made of P single propagators, then the nth prefractal generation will have 2^nP single propagators; it will correspond to the partition function of a FJC made of $N=2(1+2^{(n-1)}P)$ bonds. This fractalization looks like the reverse of the decimation method [14,6,3].

To contract the propagators further we take $x_i=\frac{1}{4}$ in (67). Thus the function $g_N^{(R)}(\mathbf{x}')$ is defined as a scalar field on a Euclidean space of a dimension smaller than the Euclidean space defined in Sec. IV B. This space has a dimension $(N-1)/2$ if N is odd, and $(N/2-1)$ if N is even.

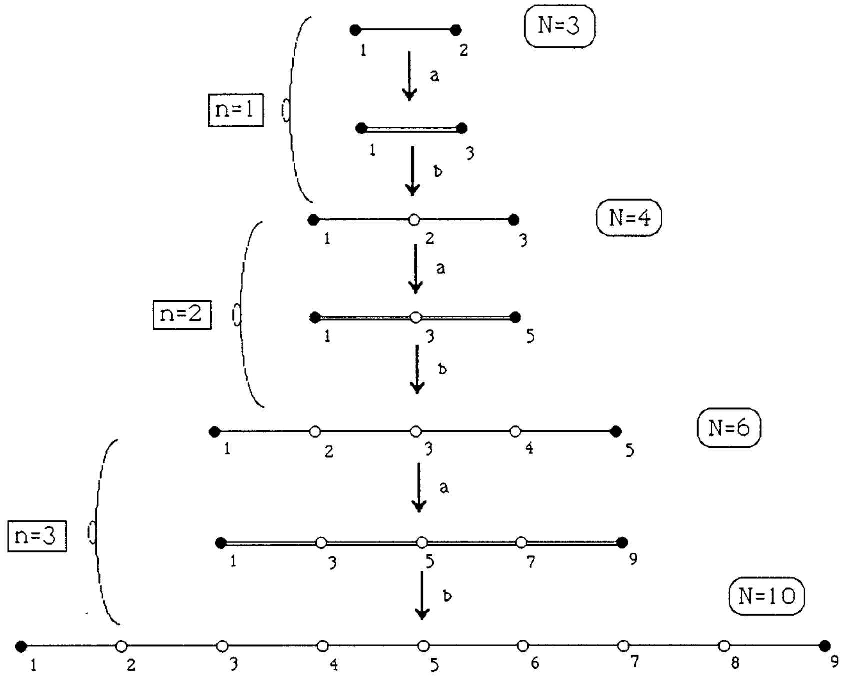

FIG. 2. Schematic representation of the first three stages associated with the building of the prefractal sequence for the butane skeleton as a fractal initiator. This looks like the reverse of the decimation method.

Relations between the hypergeometric functions give

$$F_2\left(\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2};x_1,\frac{1}{4}\right) = \sum_{n_1=0}^{\infty} \frac{1}{n_1!}\frac{(n_1,1/2)}{(n_1,d/2)}\,{}_2F_1\left(n_1+\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)x_1^{n_1} \qquad (70)$$

and

$$F_K\left(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2},\frac{d}{2};\frac{1}{4},x_1,\frac{1}{4}\right) = \sum_{n_1=0}^{\infty} {}_2F_1\left(\frac{1}{2},n_1+\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)\frac{1}{n_1!}\left(n_1,\frac{d}{2}\right) \times {}_2F_1\left(n_1+\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)x_1^{n_1}, \qquad (71)$$

where F_2 is the second Appell double hypergeometric function, and F_K the triple hypergeometric function of Lauricella-Saran (see [29]).

From Eqs. (68) and (69), we obtain derivatives of all orders of $g_N^{(R)}$ at the origin. If N is odd

$$\partial_{x_{2P}}^{n_{2P}} g_{2P+1}^{(R)}(\mathbf{x}')|_0 = g_{2P+1}^{(d)}(0)\left[{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)\right]^{(P-1)} \times \partial_{x_{2P+1}}^{n_{2P+1}}\,{}_2F_1\left(n_1+\frac{1}{2},\frac{1}{2};\frac{d}{2};x_{2P}\right)|_{x_{2P}=0} \qquad (72)$$

for $3\leqslant i\leqslant 2P-3$ (i odd) and

$$\partial_{x_i}^{n_i} g_{2P+1}^{(R)}(\mathbf{x}')|_{\mathbf{0}} = g_{2P+1}^{(d)}(0)\left[{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)\right]^{(P-3)} \times \partial_{x_i}^{n_i} F_K\left(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2},\frac{d}{2};\frac{1}{4},x_i,\frac{1}{4}\right)\Bigg|_{x_i=0} \qquad (73)$$

for $i=1$ or $2P-1$. If N is even

$$\partial_{x_i}^{n_i} g_{2P}^{(R)}(\mathbf{x}')|_{\mathbf{0}} = g_{2P}^{(d)}(0)\left[{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)\right]^{(P-2)} \times \partial_{x_i}^{n_i} F_2\left(\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2};x_i,\frac{1}{4}\right)\Bigg|_{x_i=0} \qquad (74)$$

and relations similar to Eqs. (72) and (73). As for (60), the restriction of $g_{2P+1}^{(R)}$ to each axis of the space for $|x_i|<1$ is given by

$$g_{2P+1}^{(R)}(x_{2P}\hat{\mathbf{e}}_{2P}) = g_{2P+1}^{(d)}(0)\left[{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)\right]^{(P-1)} \times {}_2F_1\left(n_1+\frac{1}{2},\frac{1}{2};\frac{d}{2};x_{2P}\right) \qquad (75)$$

for $3\leqslant i\leqslant 2P-3$ (i odd) and

$$g_{2P+1}^{(R)}(x_i\hat{\mathbf{e}}_i) = g_{2P+1}^{(d)}(0)\left[{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)\right]^{(P-3)} \times F_K\left(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2},\frac{d}{2};\frac{1}{4},x_i,\frac{1}{4}\right) \qquad (76)$$

for $i=1$ or $2P-1$. For N even

$$g_{2P}^{(R)}(x_i\hat{\mathbf{e}}_i) = g_{2P}^{(d)}(0)\left[{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)\right]^{(P-2)} \times F_2\left(\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2};x_i,\frac{1}{4}\right) \qquad (77)$$

and similar relations on the other axis.

The Feynman rules of the FJC may be used for calculations involving hypergeometric functions.

E. $J_N^{(d)}$ for small N

In this subsection, we calculate $g_N^{(d)}(\mathbf{x})$ for a few small values of the degree of polymerization.

1. Ethane skeleton (N=1)

For this molecule, since $N-1=0$, the previous calculations do not apply. However, $J_1^{(d)}$ can be computed from (32):

$$J_1^{(d)} = \int_{-\infty}^{+\infty} d\gamma_1\,\exp(-\gamma_1^2) = \Gamma\left(\frac{1}{2}\right). \qquad (78)$$

2. Propane skeleton (N=2)

The Feynman diagram associated with this molecule is $(n_1,\frac{1}{2})\bullet_{n_1}$. So we have

$$g_2^{(d)}(\mathbf{x}) = g_2^{(d)}(\mathbf{0})\sum_{n_1=0}^{\infty}\left[(n_1,\tfrac{1}{2})\bullet_{n_1}\right] = g_2^{(d)}(\mathbf{0})\,{}_2F_1(1/2,1/2;d/2;x_1), \qquad (79)$$

and consequently

$$J_2^{(d)} = g_2^{(d)}\left(\frac{1}{4}\right) = \left(\frac{1}{2}\right)\left(\frac{1}{2}\right)^{d/2}\Gamma\left(\frac{1}{2}\right) \times \left(\frac{\Gamma(1/2)}{\Gamma(d/2)}\right)\,{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right). \qquad (80)$$

3. Butane skeleton (N=3)

The Feynman diagram associated with this molecule is $\bullet_{n_1}\!-\!\bullet_{n_2}$, giving

$$g_3^{(d)}(\mathbf{x})=g_3^{(d)}(\mathbf{0})\sum_{n_1,n_2=0}^{\infty}(\bullet_{n_1}\!-\!\bullet_{n_2})$$

$$=g_3^{(d)}(\mathbf{0})F_2(1/2,1/2,1/2;d/2,d/2;x_1,x_2), \tag{81}$$

and thus

$$J_3^{(d)}=g_3^{(d)}\left(\frac{1}{4},\frac{1}{4}\right)=\left(\frac{1}{2}\right)^2\left(\frac{1}{2}\right)^d\Gamma\left(\frac{1}{2}\right)$$

$$\times\left(\frac{\Gamma(1/2)}{\Gamma(d/2)}\right)^2F_2\left(\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2};\frac{1}{4},\frac{1}{4}\right). \tag{82}$$

4. Pentane skeleton (N=4)

For this molecule the associated Feynman diagram is $\bullet_{n_1}\!-\!\circ_{n_2}\!-\!\bullet_{n_3}$. So we have

$$g_4^{(d)}(\mathbf{x})=g_4^{(d)}(\mathbf{0})\sum_{n_1,n_2,n_3=0}^{\infty}(\bullet_{n_1}\!-\!\circ_{n_2}\!-\!\bullet_{n_3})$$

$$=g_4^{(d)}(\mathbf{0})F_K\left(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2};x_1,x_2,x_3\right). \tag{83}$$

With the contractions (65) and (66), the Feynman diagram is also

$$\sum_{n_2=0}^{\infty}\bullet_{n_1}\!-\!\circ_{n_2}\!-\!\bullet_{n_3}=\bullet_{n_1}\!=\!\bullet_{n_3}. \tag{84}$$

We have

$$J_4^{(d)}=g_4^{(d)}\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$$

$$=\left(\frac{1}{2}\right)^3\left(\frac{1}{2}\right)^{3d/2}\Gamma\left(\frac{1}{2}\right)\left(\frac{\Gamma(1/2)}{\Gamma(d/2)}\right)^3$$

$$\times F_K\left(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2},\frac{d}{2};\frac{1}{4},\frac{1}{4},\frac{1}{4}\right). \tag{85}$$

5. General form for any N

We can define a multiple hypergeometric function $F_G^{(N)}$ such that

$$g_N^{(d)}(\mathbf{x})=g_N^{(d)}(\mathbf{0})F_G^{(N)}\left(\frac{1}{2},\ldots,\frac{1}{2};\frac{d}{2},\ldots,\frac{d}{2};x_1,\ldots,x_{N-1}\right). \tag{86}$$

For $x_1=\cdots=x_i=\cdots=x_{N-1}=\frac{1}{4}$, all the nontrivial dependence on the degree of polymerization of the partition function is included in $F_G^{(N)}$. This function is far from simple; however, with Eq. (60), its restriction to each axis of the Euclidean space is known. With the method of the previous subsections, we can build more and more accurate approximations of $F_G^{(N)}$ [31].

V. NUMERICAL STUDY OF $J_N^{(d)}$

To test the precision of the analytical method of the previous section, the results will be compared with a numerical calculation. A feature of the method used in Sec. IV is that it uses the dimension of the physical space in which the polymer is contained as a real parameter and not as the number of independent components of the bond vectors. To obtain another nonintegrated form of the partition function with d as a real parameter, we must not make the integration over the set of variables $\{\Omega_n\}$ before the integration over the variables $\{\hat{\mathbf{u}}_n\}$ as is done in [12], because the values allowed for d in that way would be the integer values, but the method must be generalized to noninteger values of d too. For this purpose, the integration over $\{\hat{\mathbf{u}}_n\}$ is still made before the integration over $\{\Omega_n\}$, then the Bessel functions are expressed with their representation (38), and thus the space dimension d becomes a parameter of which the partition function is a function. Then we make the complete integration over the variables $\{\omega_n\}$; this allows us to recover the metric determinant of the freely jointed chain [8,10,12], which in this way is independent of the space dimension. Since we do not know the analytical form of the integral containing this determinant, we estimate it with a Monte Carlo algorithm using importance sampling. The numerical results obtained with this algorithm permit a comparison with the approximate analytical results obtained in Sec. IV.

This section is divided into three subsections. In Sec. V A, the analytical form of $J_N^{(d)}$ is established with the metric determinant of the FJC for any dimension of space. In Sec. V B, the integral is computed with the Monte Carlo algorithm. In Sec. V C, the analytical results of Sec. IV are compared with the numerical results of Sec. V B, and an accurate approximation for the partition function of the FJC made of N bonds is given.

A. Another integral equation for $J_N^{(d)}$

To obtain the FJC metric determinant, a recurrence based on the computational rules for the determinants is used. The first stage of the recurrence is to determine $f_{N-1}^{(d)}$ from $f_N^{(d)}$. With the relation (41), $f_{N-1}^{(d)}$ is defined by

$$f_{N-1}^{(d)}=A_{N-1}\int_{-\infty}^{+\infty}d\omega_{N-1}\,\omega_{N-1}^{(1-d/2)}I_{(d/2-1)}(\omega_{N-1})$$

$$\times\exp\left(-\prod_{p=1}^{N-2}(\omega_{(N-1-p)}^2)^{(-1)^p}\omega_{N-1}^2\right)f_N^{(d)}, \tag{87}$$

which, using the integral representation of the Bessel functions (38), can be cast in the form

$$f_{N-1}^{(d)}=A_{N-1}\,\frac{(1/2)^{(d/2-1)}}{\Gamma([d-1]/2)\Gamma(1/2)}\,\frac{(1/2)^{d/2}}{\Gamma([d-1]/2)}\int_{-\infty}^{+\infty}d\omega_{N-1}\times\int_{-1}^{1}dt_{N-1}(1-t_{N-1}^{2})^{(d-3)/2}e^{(\omega_{N-1}t_{N-1})}\times\int_{0}^{1}dt_{N}(1-t_{N}^{2})^{(d-3)/2}e[-A_{N-1}^{2}(1-t_{N}^{2}/4)\omega_{N-1}^{2}]. \tag{88}$$

The integral over ω_{N-1} is Gaussian; thus

$$f_{N-1}^{(d)}=\left[\left(\frac{1}{2}\right)^{d/2}\frac{1}{\Gamma([d-1]/2)}\right]^{2}\int_{0}^{1}dt_{(N-1)}\times\int_{0}^{1}dt_{N}(1-t_{(N-1)}^{2})^{(d-3)/2}(1-t_{N}^{2})^{(d-3)/2}\times\left(\frac{1}{(1-t_{N}^{2}/4)}\right)^{1/2}\exp\left(\frac{t_{N-1}^{2}}{4(1-t_{N}^{2}/4)}\,A_{N-2}^{2}\omega_{N-2}^{2}\right). \tag{89}$$

The relation (41) permits one to find the dependence of $f_{N-1}^{(d)}$ on ω_{N-2} and thus to build a recurrence relation. Let $M^{(p)}$ be a sequence of square matrices $p\times p$, such that they verify the recurrence relation

$$\det M^{(p)}=\det M^{(p-1)}-c_{p-1}^{2}\det M^{(p-2)}, \tag{90}$$

where $\{c_{p}\}$ is a sequence of real numbers, and

$$\det M^{(1)}=1,\qquad \det M^{(2)}=1-c_{1}^{2}. \tag{91}$$

With these definitions, assume that $f_{N-p}^{(d)}$ can be written as

$$f_{N-p}^{(d)}=\left[\left(\frac{1}{2}\right)^{d/2}\frac{1}{\Gamma([d-1]/2)}\right]^{(p+1)}\times\int_{0}^{1}\prod_{n=0}^{p}dt_{(N-n)}(1-t_{(N-n)}^{2})^{(d-3)/2}\left(\frac{1}{\det M^{(p+1)}}\right)^{1/2}\times\exp\left(\frac{t_{N-p}^{2}}{4}\,\frac{\det M^{(p)}}{\det M^{(p+1)}}\,A_{N-p-1}^{2}\omega_{N-p-1}^{2}\right). \tag{92}$$

Then we have

$$f_{N-p-1}^{(d)}=A_{(N-p-1)}\left[\left(\frac{1}{2}\right)^{(d/2-1)}\frac{1}{\Gamma([d-1]/2)\Gamma(1/2)}\right]\times\int_{-1}^{1}dt_{(N-p-1)}(1-t_{(N-p-1)}^{2})^{(d-3)/2}\times\int_{-\infty}^{+\infty}d\omega_{N-p-1}\exp(\omega_{(N-p-1)}t_{(N-p-1)})\times\exp(-A_{N-p-1}^{2}\omega_{N-p-1}^{2})f_{N-p}^{(d)}. \tag{93}$$

The integral over ω_{N-p-1} is Gaussian with [cf. Eq. (15)]

$$X=\omega_{N-p-1},\qquad J=t_{N-p-1},\qquad A=2\left(1-\frac{t_{N-p}^{2}}{4}\,\frac{\det M^{(p)}}{\det M^{(p+1)}}\right)A_{N-p-1}^{2}=2\,\frac{\det M^{(p+2)}}{\det M^{(p+1)}}\,A_{N-p-1}^{2}, \tag{94}$$

and $c_{p}=\frac{1}{2}t_{N-p}$. Using the relation

$$\frac{1}{A_{N-p-1}^{2}}=A_{N-p-2}^{2}\omega_{N-p-2}^{2}, \tag{95}$$

(93) becomes

$$f_{N-p-1}^{(d)}=\left[\left(\frac{1}{2}\right)^{d/2}\frac{1}{\Gamma([d-1]/2)}\right]^{(p+2)}\int_{0}^{1}\prod_{n=0}^{p+1}dt_{(N-n)}\times(1-t_{(N-n)}^{2})^{(d-3)/2}\left(\frac{1}{\det M^{(p+2)}}\right)^{1/2}\exp\left(\frac{t_{N-p-1}^{2}}{4}\,\frac{\det M^{(p+1)}}{\det M^{(p+2)}}\,A_{N-p-2}^{2}\omega_{N-p-2}^{2}\right). \tag{96}$$

For $p=0$, the relation between $f_{N-1}^{(d)}$ [Eq. (89)] and $f_{N}^{(d)}$ is in agreement with (92) on account of the definitions (90) and (91). Equation (96) shows the stability of Eq. (92) under the recurrence, so this form is right for all $0\leqslant p\leqslant N-2$. In particular, for $p=N-2$ one has

$$f_{2}^{(d)}=\left[\left(\frac{1}{2}\right)^{d/2}\frac{1}{\Gamma([d-1]/2)}\right]^{N-1}\int_{0}^{1}\prod_{n=0}^{N-2}dt_{(N-n)}\times(1-t_{(N-n)}^{2})^{(d-3)/2}\left(\frac{1}{\det M^{(N-1)}}\right)^{1/2}\exp\left(\frac{t_{2}^{2}}{4}\,\frac{\det M^{(N-2)}}{\det M^{(N-1)}}\,\omega_{1}^{2}\right), \tag{97}$$

which by definition of $f_1^{(d)}$ and $J_N^{(d)}$ gives a Gaussian integration over ω_1 and with $x_p = t_{N-p}$

$$J_N^d = \sqrt{\pi}\left[\left(\frac{1}{2}\right)^{d/2}\frac{1}{\Gamma([d-1]/2)}\right]^{(N-1)}\int_0^1 \prod_{n=1}^{N-1} dx_n \times (1-x_n^2)^{(d-3)/2}\left(\frac{1}{\det M^{(N)}}\right)^{1/2}. \tag{98}$$

If the matrix $M^{(p)}$ is taken as

$$M^{(p)} = \begin{pmatrix} 1 & \frac{1}{2}x_1 & 0 & \cdots & 0 & 0 & 0 \\ \frac{1}{2}x_1 & 1 & \frac{1}{2}x_2 & \cdots & 0 & 0 & 0 \\ 0 & \frac{1}{2}x_2 & 1 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 1 & \frac{1}{2}x_{(p-2)} & 0 \\ 0 & 0 & 0 & \cdots & \frac{1}{2}x_{(p-2)} & 1 & \frac{1}{2}x_{(p-1)} \\ 0 & 0 & 0 & \cdots & 0 & \frac{1}{2}x_{(p-1)} & 1 \end{pmatrix}, \tag{99}$$

then it verifies the conditions (90) and (91). This result, when replaced in (31), gives the partition function of a FJC as

$$Q_N^{(d)} = \frac{1}{2}\left[\left(\frac{1}{2}\right)^{(d/2-1)}\frac{\Gamma(1/2)}{\Gamma([d-1]/2)}S_d(1)\right]V\left(\frac{m}{4\pi^2\beta\hbar^2}\right)^{d/2} \times\left[\left(\frac{1}{2}\right)^{(d+2)/(d-1)} \times\left(\frac{1}{\Gamma([d-1]/2)}\right)^{2/(d-1)}\frac{ma^2}{\beta\hbar^2}\right]^{N(d-1)/2} I_N^{(d)}, \tag{100}$$

where

$$I_N^{(d)} = \int_0^1 \prod_{n=1}^{N-1} dx_n (1-x_n^2)^{(d-3)/2}\left(\frac{1}{\det M^{(N)}}\right)^{1/2}. \tag{101}$$

It is the value of $I_N^{(d)}$ that we estimate by a Monte Carlo algorithm. In this relation d is only an integration parameter, which would not be the case if we had made the Gaussian integration over the set of variables $\{\Omega_n\}$ in Eq. (19).

B. Monte Carlo integrations

From Eq. (101), $I_N^{(d)}$ may be considered as the average value of $(1/\det M^{(N)})^{1/2}$ over the distribution $\rho_N(\mathbf{x}) = \Pi_{n=1}^{N-1} dx_n (1-x_n^2)^{(d-3)/2}$, i.e.,

$$I_N^{(d)} = \left(\int_{[0,1]^{(N-1)}} d\mathbf{x}\,\rho_N(\mathbf{x})\right)\left\langle\left(\frac{1}{\det M^{(N)}}\right)^{1/2}\right\rangle_{\rho_N(\mathbf{x})}. \tag{102}$$

Importance sampling is done over the distribution function $\rho_N(\mathbf{x})$ where d appears as a parameter. Results for noninteger values of d can thus be obtained as well. The normalization of the distribution function $\rho_N(\mathbf{x})$ is easily calculated to be

$$(N_o^{(d)})^{(N-1)} = \int_0^1 \prod_{n=1}^{N-1} dx_n (1-x_n^2)^{(d-3)/2} = \left(\frac{1}{2}\frac{\Gamma(1/2)\Gamma([d-1]/2)}{\Gamma(d/2)}\right)^{(N-1)}. \tag{103}$$

We have applied the Monte Carlo integration method to FJC's for which the number of bonds takes all values between $N=2$ and 500 and considered 28 values of d between 2 and 8 (including noninteger dimensions). For each value of d, 499 partition functions of the FJC have been obtained. The Monte Carlo results are shown in Fig. 3. The data may be very well represented by a straight line fit

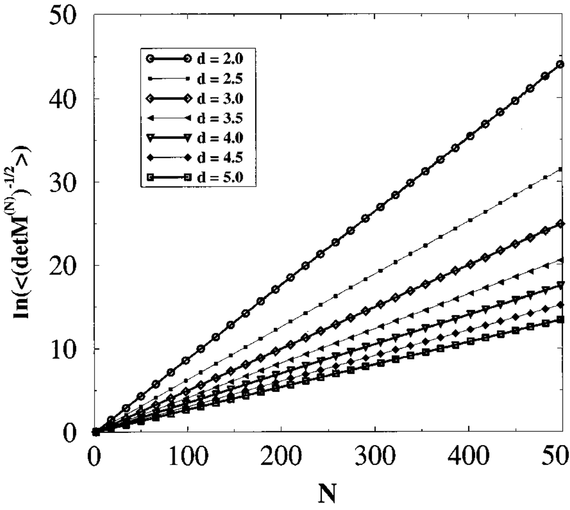

FIG. 3. Results obtained for $\ln\langle(1/\det M^{(N)})^{1/2}\rangle_{\rho_N(\mathbf{x})}$ with a Monte Carlo algorithm using importance sampling. The straight line fit is not represented on the curves. The symbols are placed every 15 points.

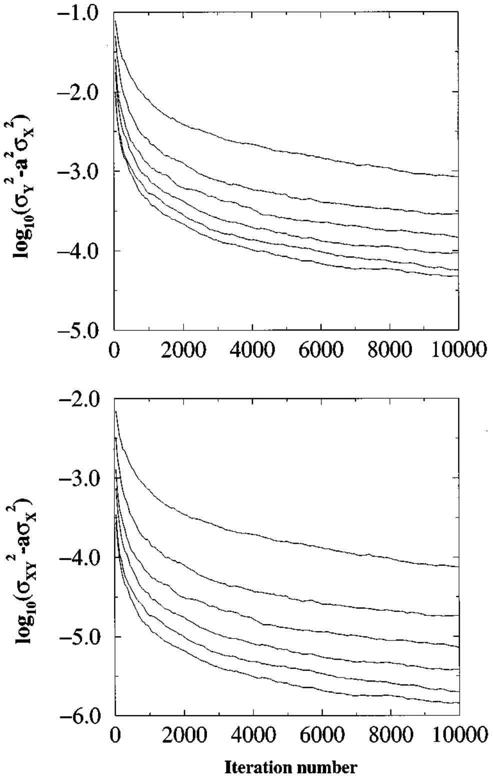

FIG. 4. Accuracy of the straight line fit for data from Fig. 3 versus number of Monte Carlo iterations. On both graphs the first curve from the top corresponds to $d=2.0$, and the following curves are obtained by increasing d by 0.5; thus on both graphs the lowest curve corresponds to $d=4.5$.

$$\ln\left\langle\left(\frac{1}{\det M^{(N)}}\right)^{1/2}\right\rangle_{\rho_N(\mathbf{x})}=\ln B^{(d)}+N\ln A^{(d)}. \tag{104}$$

After only a few thousand Monte Carlo iterations, almost all the points of Fig. 3 are in agreement with the straight line fit to within 1–3 %, except for the point with $N=3$. However, for $N=3$, the analytical function $J_3^{(d)}$ is given by Eq. (85).

If correlations between two random variables (X,Y) are exactly according to a straight line fit, one has, with $\sigma_{uv}^2=\langle uv\rangle-\langle u\rangle\langle v\rangle$ and $Y=aX+b$,

$$\begin{aligned}&\sigma_Y^2-a^2\sigma_X^2=0,\\&\sigma_{XY}^2-a\sigma_X^2=0.\end{aligned} \tag{105}$$

In Fig. 4, $\log_{10}(\sigma_Y^2-a^2\sigma_X^2)$ and $\log_{10}(\sigma_{XY}^2-a\sigma_X^2)$ are shown as functions of the number of Monte Carlo integrations. The accuracy of the fit is so good than after only a few thousand iterations, the differences between σ_Y^2 and $a^2\sigma_X^2$, and σ_{XY}^2 and $a\sigma_X^2$, are less than 0.01. Thus the approximation

$$I_N^{(d)}=\frac{B^{(d)}}{N_o^{(d)}}\,(N_o^{(d)}A^{(d)})^N \tag{106}$$

appears to be extremely good. The results for $A^{(d)}$ and $B^{(d)}$ for several values of d are given in Table I.

C. Analytical form for the partition function of the FJC

From the results of the previous subsection, the accuracy of the analytical expressions presented in Sec. IV can be tested on the coefficients of the fit. The partition function of the FJC is given by

$$Q_N^{(d)}(V,T)=q_o^{(d)}Q_\diamond^{(d)}(V,T)\left(\frac{T}{T_o(d)}\right)^{N(d-1)/2}, \tag{107}$$

with

$$\begin{aligned}q_o^{(d)}&=\left(\frac{\pi}{2}\right)^{1/2}\frac{B^{(d)}}{\Gamma([d-1]/2)^2},\\ Q_\diamond^{(d)}(V,T)&=\left(\frac{mkT}{4\pi^2\hbar^2}\right)^{1/2}V,\\ \beta_o(d)&=\frac{1}{kT_o(d)}=\left(\frac{1}{2}\right)^{(d+4)/(d-1)}\\&\quad\times\left(A^{(d)}\frac{\Gamma(1/2)}{\Gamma(d/2)}\right)^{2/(d-1)}\frac{ma^2}{\hbar^2}.\end{aligned} \tag{108}$$

In Fig. 5, $A^{(d)}$ and $B^{(d)}$ are shown as functions of d. From Sec. IV B, the scalar field $h_1(\mathbf{x})$ defined by

$$h_1(\mathbf{x})=g_N^{(d)}(\mathbf{0})\,{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};x_{N-1}\right)\prod_{i=1}^{(N-2)}{}_1F_1\left(\frac{1}{2};\frac{d}{2};x_i\right) \tag{109}$$

coincides with the field $g_N^{(d)}$ on each axis. Furthermore, from Sec. IV D, the scalar field $h_1^{(R)}(\mathbf{x}')$ defined by

$$\begin{aligned}h_1^{(R)}(\mathbf{x}')=&\,g_{2P+1}^{(d)}(\mathbf{0})F_2\left(\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2};x_1,\frac{1}{4}\right)\\&\prod_{i=3,\mathrm{odd}}^{2P-3}F_K\left(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2},\frac{d}{2};\frac{1}{4},x_i,\frac{1}{4}\right)\\&\times F_2\left(\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2};\frac{1}{4},x_{2P-1}\right)\\&\times{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};x_{2P+1}\right)\end{aligned} \tag{110}$$

coincides with the field $g_{2P+1}^{(R)}$ on each axis. Of course, $h_1(\mathbf{x})$ and $h_1^{(R)}(\mathbf{x}')$ are not exactly equal to the fields $g_N^{(d)}$ and $g_{2P+1}^{(R)}$ away from the axis, but they may serve as approximations of these fields. The difference between Secs. IV and V resides only in the integration order in which the integrals have been computed. As the integrals are convergent, both results must be equal. Thus, by fixing the value of the fields $h_1(\mathbf{x})$ and $h_1^{(R)}(\mathbf{x}')$ at $x_1=\cdots=x_i=\cdots=x_{N-1}=\frac{1}{4}$, after simplification, one has the following.

For h_1

$$B^{(d)}(A^{(d)})^N={}_2F_1({}_1F_1)^{(N-2)}, \tag{111}$$

giving

TABLE I. The numerical values of the coefficients $A^{(d)}$ and $B^{(d)}$ from the straight line fit of the Monte Carlo estimates of $I_N^{(d)}$ and the analytical approximations of both coefficients [we use the reduced notations $({}_1F_1)={}_1F_1(1/2,d/2,1/4)$ and $({}_2F_1)={}_2F_1(1/2,1/2,d/2,1/4)$].

d	$A^{(d)}$	$B^{(d)}$	$({}_1F_1)$	$({}_2F_1)$	$\frac{({}_1F_1)}{({}_2F_1)^2}$	$({}_2F_1)^{-1}$	$({}_1F_1)^{-1}$
2.0	1.092(5)	0.894(0)	1.137 58	1.073 18	0.829 297	0.931 81	0.879 06
2.2	1.077(9)	0.912(7)	1.124 50	1.066 00	0.843 021	0.938 09	0.889 28
2.4	1.069(0)	0.921(8)	1.113 65	1.060 07	0.854 745	0.943 33	0.897 95
2.5	1.065(3)	0.928(3)	1.108 90	1.057 48	0.859 978	0.945 64	0.901 79
2.6	1.061(9)	0.932(4)	1.104 51	1.055 09	0.864 872	0.947 79	0.905 38
2.8	1.056(1)	0.938(0)	1.096 71	1.050 85	0.873 691	0.951 61	0.911 82
3.0	1.051(3)	0.944(9)	1.089 97	1.047 20	0.881 453	0.954 93	0.917 46
3.2	1.047(2)	0.949(3)	1.084 10	1.044 02	0.888 320	0.957 84	0.922 42
3.4	1.043(8)	0.952(4)	1.078 94	1.041 24	0.894 454	0.960 39	0.926 84
3.5	1.042(2)	0.955(3)	1.076 58	1.039 97	0.897 279	0.961 57	0.928 87
3.6	1.040(7)	0.956(5)	1.074 36	1.038 78	0.899 960	0.962 67	0.930 79
3.8	1.038(1)	0.959(0)	1.070 28	1.036 59	0.904 928	0.964 70	0.934 33
4.0	1.035(8)	0.962(0)	1.066 62	1.034 63	0.909 422	0.966 53	0.937 54
4.2	1.033(2)	0.964(5)	1.062 54	1.032 45	0.914 486	0.968 57	0.941 14
4.5	1.031(0)	0.967(7)	1.058 92	1.030 53	0.919 042	0.970 37	0.944 36
5.0	1.027(3)	0.971(4)	1.052 81	1.027 28	0.926 810	0.973 44	0.949 84
6.0	1.022(1)	0.972(7)	1.043 70	1.010 87	0.927 988	0.989 25	0.958 13
7.0	1.018(5)	0.981(1)	1.037 26	1.019 09	0.947 194	0.981 27	0.964 08
8.0	1.015(8)	0.983(5)	1.032 46	1.016 59	0.953 671	0.983 68	0.968 56

$$A^{(d)}=({}_1F_1),\qquad B^{(d)}=({}_2F_1)/({}_1F_1)^2. \tag{112}$$

For $h_1^{(R)}$, when $N=2P+1$,

$$B^{(d)}(A^{(d)})^{(2P+1)}=(F_2)^2({}_2F_1)(F_K)^{(P-1)}, \tag{113}$$

giving

$$A^{(d)}=(F_K)^{1/2},\qquad B^{(d)}=(F_2)^2({}_2F_1)/(F_K)^{3/2}, \tag{114}$$

and for $h_1^{(R)}$, when $N=2P$,

$$B^{(d)}(A^{(d)})^{2P}=(F_2)^2(F_K)^{(P-1)}, \tag{115}$$

leading to

$$A^{(d)}=(F_K)^{1/2},\qquad B^{(d)}=(F_2)^2/(F_K), \tag{116}$$

where the arguments of the hypergeometric functions have been omitted.

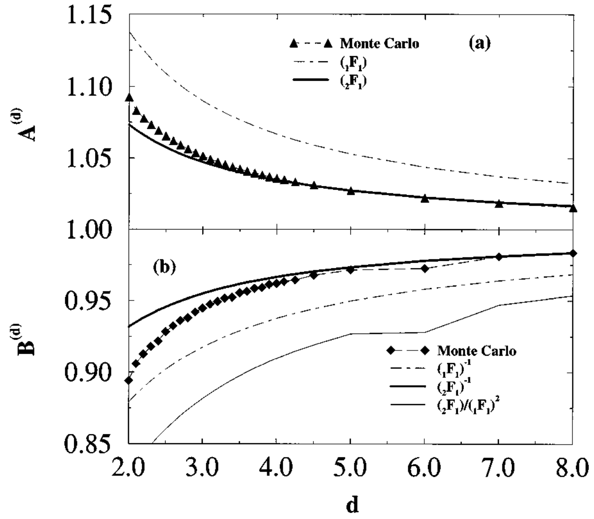

FIG. 5. Comparison between the theoretical values for $A^{(d)}$ and $B^{(d)}$ obtained with an approximation of the function $g_N^{(d)}$ and the values of $A^{(d)}$ and $B^{(d)}$ obtained from the straight line fit of the Monte Carlo data. The numerical values are given in Table I. We use the reduced notations $({}_1F_1)={}_1F_1(1/2;d/2;1/4)$ and $({}_2F_1)={}_2F_1(1/2,1/2;d/2;1/4)$.

In Eqs. (114) and (116) the odd-even effect appears explicitly in the value of $B^{(d)}$. In both equations $A^{(d)}$ takes identical values. Thus with the use of the approximation given by Eqs. (107) and (108) the odd-even effect must decrease when the degree of polymerization increases. This is in agreement with the results of Fisher and Hiley [15] and those of Grassberger and Hegger [16].

With the relations

$$F_2\left(\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2};0,\frac{1}{4}\right)={}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right) \tag{117}$$

and

$$F_K\left(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2};\frac{d}{2},\frac{d}{2},\frac{d}{2};\frac{1}{4},0,\frac{1}{4}\right)={}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right)\,{}_2F_1\left(\frac{1}{2},\frac{1}{2};\frac{d}{2};\frac{1}{4}\right) \tag{118}$$

the odd-even effect is canceled and another approximation is possible. To zeroth order, with the scalar field $g_N^{(d)}$, it gives

$$A^{(d)} \approx ({}_1F_1) \quad \text{and} \quad B^{(d)} \approx ({}_1F_1)^{-1}, \tag{119}$$

and to first order, with the scalar field $g_N^{(R)}$, it gives

$$A^{(d)} \approx ({}_2F_1) \quad \text{and} \quad B^{(d)} \approx ({}_2F_1)^{-1}. \tag{120}$$

In Table I, the values of Eqs. (119) and (120) are reported, as well as those of Eq. (112). In Fig. 5, these analytical approximations are shown as functions of d. The good agreement between these results confirms the validity of the method described in Sec. IV and the approximation (107) made for the partition function of the FJC.

Finally, the asymptotic behavior for $d \to \infty$ gives ${}_1F_1(1/2;d/2;1/4) \to 1$ and ${}_2F_1(1/2,1/2;d/2;1/4) \to 1$. In this limit, the only nonzero contribution to $I_N^{(d)}$ is given by $\mathbf{x}=\mathbf{0}$; then

$$\left\langle \left(\frac{1}{\det M^{(N)}} \right)^{1/2} \right\rangle_{\rho N(\mathbf{x})} \to 1,$$

and $A^{(d)} \to 1$ and $B^{(d)} \to 1$. With the approximation (107) for the partition function the study of the thermodynamical and statistical properties is straightforward.

VI. THERMODYNAMICAL AND STATISTICAL PROPERTIES OF FJC's

The two preceeding sections give the canonical partition function of the FJC. Then it is possible to study the equilibrium thermodynamical properties of a gas made of M FJC's. As explained in the Introduction and explicitly used in Eqs. (10) and (11), the FJC can be considered as an ideal gas with phase space φ_{rest}. It is straightforward to build the microcanonical and grand canonical ensembles relative to this ideal gas via Laplace transform. The meaning of the partition function permits one to give the connection with random walks and to compute the critical exponents γ and ν.

A. Gas of FJC's in the canonical ensemble

The canonical partition function (107) of the FJC permits one to express the canonical partition function of a gas of M FJC's as

$$\begin{aligned} Z_N^{(d)}(M,V,T) &= \frac{1}{M!} [Q_N^{(d)}(V,T)]^M \\ &= \frac{1}{M!} (q_o^{(d)})^M [Q_\diamond^{(d)}(V,T)]^M \\ &\quad \times \left(\frac{T}{T_o(d)} \right)^{(MN/2)(d-1)}. \end{aligned} \tag{121}$$

The free energy of the gas of FJC's is given by

$$\begin{aligned} F_N^{(d)}(M,V,T) &= -kT \ln[Z_N^{(d)}(M,V,T)] \\ &= kT \ln(M!) - M\xi_N^{(d)}(V,T), \end{aligned} \tag{122}$$

where $\xi_N^{(d)}(V,T)$ is the free energy of one FJC,

$$\begin{aligned} \xi_N^{(d)}(V,T) &= \xi_{\text{ex}}^{(d)}(V,T) - kT \ln[Q_o^{(d)}(V,T)] - kT \ln(q_o^{(d)}), \\ \xi_{\text{ex}}^{(d)}(V,T) &= (N/2)(d-1)kT \ln(T_o(d)/T). \end{aligned} \tag{123}$$

The average energy of the gas is given by

$$\overline{E_c} = -\frac{\partial \ln Z_N^{(d)}}{\partial \beta}\bigg|_{M,V} = M\overline{e_c} = MkT\left(\frac{d}{2} + \frac{N}{2}(d-1) \right). \tag{124}$$

Equation (124) shows that equipartition is verified, as was already obvious from Eq. (31) of Sec. III. The entropy is given by

$$S_N^{(d)}(M,V,T) = \frac{1}{T} [\overline{E_c} - F_N^{(d)}(M,V,T)], \tag{125}$$

$$S_N^{(d)}(M,V,T) = S_{\text{id}}^{(d)}(M,V,T) + Ms_N^{(d)}(T), \tag{126}$$

where

$$\begin{aligned} S_{\text{id}}^{(d)}(M,V,T) &= k\left(\frac{d}{2} M + M \ln[Q_\diamond^{(d)}(V,T)] - \ln(M!) \right), \\ s_N^{(d)}(T) &= k\left(\frac{N}{2}(d-1) + \ln(q_o^{(d)}) - s_{\text{ex}}^{(d)}(T) \right), \\ s_{\text{ex}}^{(d)}(T) &= \frac{N}{2}\left[(d-1)\ln\left(\frac{T_o(d)}{T} \right) \right]. \end{aligned} \tag{127}$$

The relations (127) are the Sakur-Tetrode relation for the FJC. In Fig. 6, $s_{\text{ex}}^{(d)}(T)$ and $\xi_{\text{ex}}^{(d)}(V,T)$ are shown as functions of $T^* = T/T_o(d)$ for a few values of the degree of polymerization and $d=3$. As long as the size of the box is greater than the typical size of the polymer [6], the equation of state of the gas of FJC's is the same as that of an ideal monatomic gas, $PV=MkT$. The chemical potential is given by

$$\begin{aligned} \mu_N^{(d)} &= F_N^{(d)}(M+1,V,T) - F_N^{(d)}(M,V,T) \\ &= kT \ln(M+1) - \xi_N^{(d)}(V,T). \end{aligned} \tag{128}$$

This chemical potential may serve as a reference value for the computation of chemical potentials in realistic models, with the configurational bias method [32–34].

Considering that the FJC is an ideal gas with phase space φ_{rest}, the degree of polymerization can be associated with a second chemical potential χ called the bonding chemical potential. In the canonical ensemble, χ is given by

$$\chi = \xi_{N+1}^{(d)}(V,T) - \xi_N^{(d)}(V,T) = \frac{1}{2}(d-1)kT \ln\left(\frac{T_o(d)}{T} \right). \tag{129}$$

With N and χ, thermodynamical ensembles of the same kind as the grand canonical ensemble may be associated [41]. This second chemical potential has been used previously by de Gennes [3,35] and Redner and Reynolds [36] in a study of SAW's, Daoud and Family [37] in a study of polydispersity, Grassberger and Hegger [38] in simulations of a polymer, and by many others (for a review, see [4]). In a recent work, Gujrati [40] has used several chemical potentials of this kind

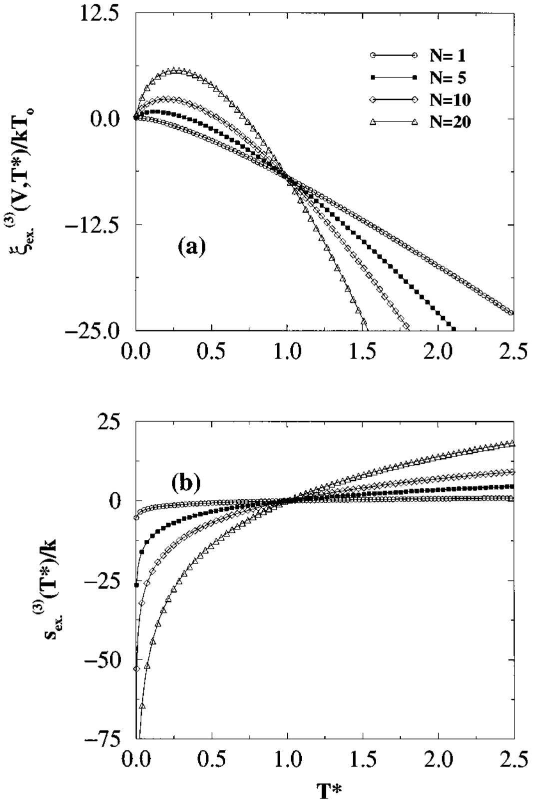

FIG. 6. (a) Excess free energy $\xi_{ex}^{(3)}(V,T)$ for a FJC of a few different degrees of polymerization as a function of $T^*=T/T_o(d)$. (b) Excess entropy $s_{ex}^{(3)}(T)$ for FJC's as in (a).

to give a geometrical description of the phase transitions and has applied this formalism to branched polymers.

In most of the previous works, the authors perform calculations on lattices using a grand canonical ensemble in which the number of bonds in the polymer can fluctuate. In the present work, χ is the continuous version of these chemical potentials. The definition of χ is neither a constraint to the geometry of a regular lattice nor a particular dimension of the physical space.

B. Some thermodynamical ensembles for the FJC

In this subsection, the FJC is considered as an ideal gas with phase space φ_{rest}. From the canonical partition function of this gas, seven other thermodynamical ensembles may be built using Laplace transforms [41].

The extensive variables are (N,V,S) and the associated intensive variables are $(\chi,-P,T)$. The canonical partition function $Q_N^{(d)}(V,T)$ is obtained with an approximation on the size of the box containing the polymer. The dependence on V in $Q_N^{(d)}(V,T)$ is only linear; thus the Laplace transforms for the conjugated variables V and $-P$ are straightforward and do not give any extra information.

In Fig. 7, all the isochoric ensembles are shown in equilibrium with their reservoirs. We study two of these ensembles, the microcanonical ensemble partly studied to some extent by Edwards and Goodyear [9] and the grand canonical ensemble in which the conjugated variables are (N,χ).

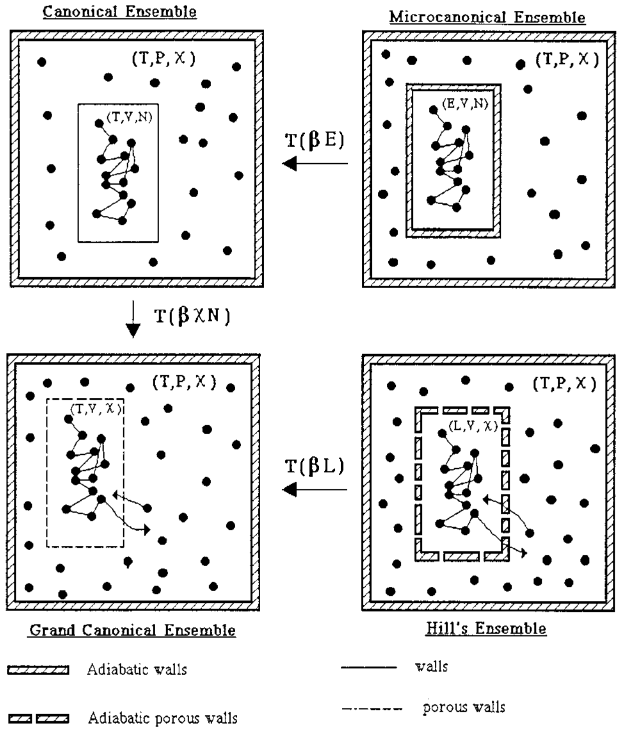

FIG. 7. Schematic representation of all isochoric thermodynamical ensembles of the FJC in equilibrium with their reservoirs. Arrows with $T(\beta xX)$ symbolize Laplace transforms according to $f(x)=\beta\int_0^{+\infty}dX\,\exp(\beta xX)F(X)$.

1. The microcanonical ensemble

From the canonical partition function $Q_N^{(d)}(V,T)$, given by Eq. (107), the microcanonical partition function is obtained by the Laplace transform

$$Q_N^{(d)}(V,T)=\beta\int_0^{+\infty}dE\;e^{-\beta E}\Omega_N^{(d)}(V,E). \qquad (130)$$

A straightforward calculation gives

$$\Omega_N^{(d)}(V,E)=\omega_o^{(d)}\Omega_\diamond^{(d)}(V,E)\,\frac{[\beta_o(d)E]^{N(d-1)/2}}{\Gamma([N(d-1)+d]/2+1)}, \qquad (131)$$

where

$$\begin{aligned}\omega_o^{(d)}&=q_o^{(d)},\\ \Omega_\diamond^{(d)}(V,E)&=\left(\frac{mE}{2\pi\hbar^2}\right)^{d/2}V.\end{aligned} \qquad (132)$$

$\Omega_N^{(d)}(V,E)$ is the number of microstates of a FJC made of N bonds isolated in a volume V with an energy E. In the work of Edwards and Goodyear the contribution $\Omega_\diamond^{(d)}(V,E)$ due to the motion of the first monomer is absent, the calculations having been done in the frame where this monomer is at rest. If we omit this contribution we recover, for $d=3$, the same behavior with E as found by these authors, which is a consequence of the equipartition.

The behavior with N is not trivial because of the presence of the gamma function.

The entropy is given by

$$\begin{aligned} s_N^{(d)} &= k\ \ln\Omega_N^{(d)}(N,E) \\ &= s_{\rm id}^{(d)} + \frac{N}{2}\,(d-1)\ln[\beta_o(d)E] \\ &\quad + k\ \ln\ \omega_o^{(d)} - k\ \ln\Gamma\left(\frac{N(d-1)+d}{2}+1\right), \end{aligned} \tag{133}$$

where $s_{\rm id}^{(d)}$ is the entropy of an ideal monomer. In the microcanonical ensemble the temperature is defined by $1/T = (\partial s_N^{(d)}/\partial E)|_{N,V}$ which leads to (124) and again to equipartition.

2. Grand canonical ensemble with respect to variables (χ,N)

This ensemble is called the grand canonical ensemble by some authors [3,4], and the equilibrium ensemble by others [39] to distinguish it from the truly grand canonical ensemble where the number of polymers can fluctuate. In this ensemble the partition function is given by

$$\Xi^{(d)}(\chi,V,T) = \sum_{N=0}^{\infty} Q_N^{(d)}(V,T)e^{\beta\chi N}, \tag{134}$$

where, for $N=0$, $Q_0^{(d)}(V,T) = q_o^{(d)} Q_\diamondsuit^{(d)}(V,T)$.

In [6], the function $\Xi^{(d)}(\chi,V,T)$ is called the generating function. In Eq. (134) the first contribution to the sum cannot be given by a single monomer, because the first monomer must have the ability to be a polymer initiator for the polymerization (see Sec. IV C). This is the reason why there is a factor $q_o^{(d)}$ in the definition of $Q_0^{(d)}(V,T)$. This factor $q_o^{(d)}$ is the continuous version of the activity for creating a chain end [6,42].

With the use of Eqs. (108), the partition function is given by

$$\Xi^{(d)}(\chi,V,T) = Q_0^{(d)}(V,T)\sum_{N=0}^{\infty}\left[\exp(\beta\chi)\left(\frac{\beta_o(d)}{\beta}\right)^{(d-1)/2}\right]^N. \tag{135}$$

The series (135) are geometrics, as for Bose-Einstein statistics [43]. $\Xi^{(d)}$ is defined only if $\chi < \chi_{\rm max}^{(d)}(T)$ where $\chi_{\rm max}^{(d)}(T)$ is given by

$$\chi_{\rm max}^{(d)}(T) = kT\,\frac{(d-1)}{2}\,\ln\left(\frac{T_o(d)}{T}\right). \tag{136}$$

$\chi_{\rm max}^{(d)}(T)$ is the continuous analog of the critical value of the activity appearing in the study of SAW's in the equilibrium ensemble [36,38,39]. The case of the subcritical phase is the only case studied in this work. When χ approaches $\chi_{\rm max}^{(d)}(T)$ a careful study is needed for two reasons, which are (a) the limitation of the box size [36,45] and (b) exchange between the system and its reservoir.

For $\chi < \chi_{\rm max}^{(d)}(T)$, the grand partition function is

$$\Xi^{(d)}(\chi,V,T) = \frac{Q_0^{(d)}(V,T)}{1-\exp(\chi/kT)(T/T_o(d))^{(d-1)/2}}, \tag{137}$$

and the grand potential

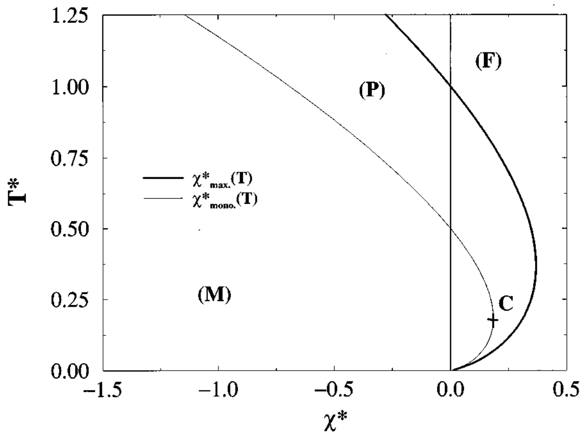

FIG. 8. Diagram of the different domains of the FJC in the plane (χ^*, T^*), with $\chi^* = \chi/kT_o(3)$ and $T^* = T/T_o(3)$. The domains are (M) the monatomic domain, (P) the polyatomic domain, and (F) the forbidden zone. The point C is like a double critical point whose coordinates are $T_c^* = (1/2e)^{2/(3-1)}$ and $\chi_c^* = [(3-1)/2]T_c^*$.

$$\begin{aligned} J^{(d)} &= -kT\ \ln Q_0^{(d)}(V,T) + kT \\ &\quad \times \ln\left[1-\exp\left(\frac{\chi}{kT}\right)\left(\frac{T}{T_o(d)}\right)^{(d-1)/2}\right]. \end{aligned} \tag{138}$$

The average number of bonds in the FJC is

$$\overline{N^{(d)}} = \frac{1}{\beta}\frac{\partial\ \ln\ \Xi^{(d)}}{\partial\chi}\bigg|_{V,T} = \frac{\exp(\chi/kT)(T/T_o(d))^{(d-1)/2}}{1-\exp(\chi/kT)(T/T_o(d))^{(d-1)/2}}. \tag{139}$$

Applying the operator $(1/\beta)(\partial/\partial\chi)$ to (139) once more gives the fluctuations $\Delta\overline{N^{(d)}}$ for the average number $\overline{N^{(d)}}$ of the bonds in the FJC. An elementary computation gives

$$\frac{\Delta\overline{N^{(d)}}}{\overline{N^{(d)}}} = \exp\{\beta[\chi - \chi_{\rm max}^{(d)}(T)]\} < 1. \tag{140}$$

In the plane (χ,T) three domains are easily identified. If $\overline{N^{(d)}} < 1$, then on average there is only one monomer in the polymer; this leads to the definition of $\chi_{\rm mono}^{(d)}(T)$ as

$$\chi_{\rm mono}^{(d)}(T) = kT\ \ln\left(\frac{1}{2}\right) + kT\,\frac{(d-1)}{2}\,\ln\left(\frac{T_o(d)}{T}\right). \tag{141}$$

The domain where $\chi < \chi_{\rm mon}^{(d)}(T)$ is the monatomic domain. If $\chi_{\rm mono}^{(d)}(T) < \chi < \chi_{\rm max}^{(d)}(T)$, then the FJC is made of several bonds; this domain is the polyatomic domain. When $\chi \to \chi_{\rm max}^{(d)}(T)$ then $\overline{N^{(d)}} \to \infty$; a FJC of infinite length is found as in [36]. This phenomenon is similar to the Bose condensation since $\chi_{\rm max}^{(d)}(T)$ is defined with the same criterion [43]. The domain $\chi > \chi_{\rm max}^{(d)}(T)$ is forbidden since the series (134) are divergents. The forbidden domain is an artifact of the limiting case studied here where the size of the box is considered to be larger than the typical size of the FJC. If ones take into account the finite size of the box then the forbidden domain disappears and the series (134) is convergent for all values of χ [45]. These three domains are shown in Fig. 8. In

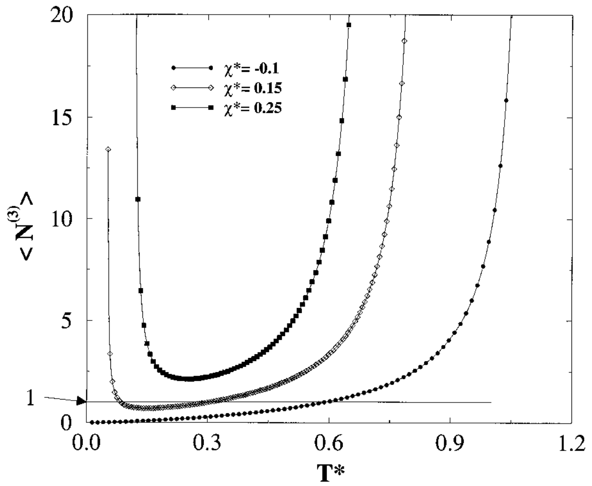

FIG. 9. Average number of links $\overline{N^{(3)}}$ in a FJC studied in the internal grand canonical ensemble as a function of $T^*=T/T_o(3)$ for different values of $\chi^*=\chi/kT_o(3)$. For $\chi^*=0.15$, polyatomic behavior is reentrant while for $\chi^*<0$ it is not. For $\chi^*=0.25$ monatomic behavior is absent.

Fig. 9 $\overline{N^{(d)}}$ is shown as a function of $T^*=T/T_o(d)$ for a few values of $\chi^*=\chi/kT_o(d)$. The coordinates of the point marked C in Fig. 8 are given by

$$T_c^*=\left(\frac{1}{2e}\right)^{2/(d-1)},$$

$$\chi_c^*=\frac{(d-1)}{2}\,T_c^*. \tag{142}$$

In Fig. 8, the polyatomic domain is reentrant; the C point is similar to the double critical point found in some binary mixtures [17]. The polyatomic domain appears strange. In this domain for $\chi_{\rm mono}^{(d)}(T)<\chi<\chi_{\rm max}^{(d)}(T)$, Eq. (140) gives $1/2<\Delta\overline{N^{(d)}}/\overline{N^{(d)}}<1$, and thus predicts large fluctuations in this domain, of the size of the whole system. The results for $\Delta\overline{N^{(d)}}/\overline{N^{(d)}}$ indicate important polydispersity in this domain. These large values of $\Delta\overline{N^{(d)}}/\overline{N^{(d)}}$ may be an artifact of the approximation on the size of the box.

C. Statistical properties and critical exponents

The exponent γ is the first exponent that we compute. This exponent is related to the total number of conformations of the FJC [44]. A FJC can be related to a random walk with the partition function interpreted as the total number of conformations of the FJC. The total number of random walks made of N steps $\mathfrak{R}_N$ is identified with $Q_N^{(d)}$; thus with

$$\mathfrak{R}_N\rightarrow Q_N^{(d)}\simeq Az^N N^{\gamma-1} \tag{143}$$

one has, using Eq. (108),

$$A=q_o Q_\diamond^{(d)}(V,T),$$

$$z=\left(\frac{T}{T_o(d)}\right)^{(d-1)/2},$$

$$\gamma=1. \tag{144}$$

A is a constant, z is the coordination number of the lattice on which the random walk is performed, and γ the critical exponent. Thus, for the FJC, the same value for the exponent γ is found as for the Gaussian polymer model.

The exponent ν is related to the size of the polymer. The distance between two distinct monomers of the same FJC is given by $|\mathbf{R}_{(n,p)}|$ where

$$\mathbf{R}_{(n,p)}=a\sum_{k=n}^{p}\hat{\mathbf{u}}_k \quad (n<p). \tag{145}$$

$\mathbf{R}_{(n,p)}$ is the bond vector between monomer $(n-1)$ and p. The square distance is

$$(\mathbf{R}_{(n,p)})^2=a^2\left(\sum_{k=n}^{p}\hat{\mathbf{u}}_k^2+2\sum_{n\leqslant i<j\leqslant p}\hat{\mathbf{u}}_i\cdot\hat{\mathbf{u}}_j\right) \tag{146}$$

and its average value

$$\langle(\mathbf{R}_{(n,p)})^2\rangle=a^2(p-n)\left(1+\frac{2}{p-n}\sum_{n\leqslant i<j\leqslant p}\langle\hat{\mathbf{u}}_i\cdot\hat{\mathbf{u}}_j\rangle\right). \tag{147}$$

With the results of Sec. III, the correlations between the bonds i and j are given by

$$\begin{aligned}\langle\hat{\mathbf{u}}_i\cdot\hat{\mathbf{u}}_j\rangle=&\frac{Q(\beta)}{Q_N^{(d)}}\int\prod_{n=1}^{N}d\Omega_n\\&\times\exp\left(-\frac{ma^2}{\beta}\sum_{n=1}^{N}\Omega_n^2\right)\int\prod_{n=1}^{N}d\hat{\mathbf{u}}_n\delta(\hat{\mathbf{u}}_n^2-1)\hat{\mathbf{u}}_i\cdot\hat{\mathbf{u}}_j\\&\times\exp\left[\frac{ma^2}{\beta}\left(\sum_{n=1}^{N-1}(\Omega_n\hat{\mathbf{u}}_n)\cdot(\Omega_{n+1}\hat{\mathbf{u}}_{n+1})\right)\right],\end{aligned} \tag{148}$$

leading, after some algebra, to

$$\begin{aligned}\langle\hat{\mathbf{u}}_i\cdot\hat{\mathbf{u}}_j\rangle=\frac{G_{ij}^{(d)}}{J_n^{(d)}}=&\frac{1}{J_n^{(d)}}\int\prod_{n=1}^{N}d\gamma_n\prod_{n\in I}(\gamma_n\gamma_{n+1})^{(1-d/2)}\\&\times I_{(d/2-1)}(\gamma_n\gamma_{n+1})\prod_{k\in J}(\gamma_k\gamma_{k+1})^{(1-d/2)}\\&\times I_{d/2}(\gamma_k\gamma_{k+1})\exp\left(-\sum_{n=1}^{N}\gamma_n^2\right),\end{aligned} \tag{149}$$

where $I=\{1,i-1\}\cup\{j+1,N\}$ and $J=\{i,j\}$. The transformation (33) gives

$$\begin{aligned}G_{ij}^{(d)}=&\int\prod_{n=1}^{N}d\omega_n|\det[J_a(\omega)]|\prod_{n\in I}(\omega_n)^{(1-d/2)}I_{(d/2-1)}(\omega_n)\\&\times\prod_{k\in J}(\omega_k)^{(1-d/2)}I_{(d/2)}(\omega_k)\exp\left(-\sum_{n=2}^{N}A_n^2\omega_n^2-\omega_1^2\right).\end{aligned} \tag{150}$$

All the permutations of the variables $\{\omega_j\}$ are not allowed because the memory effect in the FJC is included in the factor A_n^2. However, taking $E(A)$ as the number of elements in the set A, the relation (41) allows the σ permutations such that $\mathscr{C}(\sigma^*[J])=\mathscr{C}[J]$ and if $(n_1,n_2)\in(\sigma^*[J])^2$ all natural numbers between n_1 and n_2 are in the image ensemble $\sigma^*[J]$ of J with the permutation σ. This limitation on the permutations allows the correlations between the monomers i and j to propagate on the polymer, and this property must be the same anywhere in the polymer. If a permutation of this type is done in (150), $G_{ij}^{(d)}$ is invariant because $|\det(\sigma)|=1$. Moreover, since it is right for any permutation which has these properties, it is right for the permutation which puts i on 1 and j on $\mathscr{C}(J)$. Thus the invariance by propagation on the polymer imposes the relation

$$G_{ij}^{(d)}=G_{|i-j|}^{(d)}=G_{\Delta n}^{(d)} \tag{151}$$

and Eq. (147) becomes

$$\langle(\mathbf{R}_{(n,p)})^2\rangle=a^2(p-n)\left[1+\frac{2}{(p-n)J_N^{(d)}}\sum_{n\leqslant i<j\leqslant p}G_{ij}^{(d)}\right], \tag{152}$$

$$\langle(\mathbf{R}_{(n,p)})^2\rangle=a^2(p-n)\left[1+\frac{2}{J_N^{(d)}}\sum_{\Delta n=1}^{(p-n)}G_{\Delta n}^{(d)}-\frac{2}{J_N^{(d)}}\sum_{\Delta n=1}^{(p-n)}\frac{\Delta n}{p-n}G_{\Delta n}^{(d)}\right].$$

Section IV gives

$$G_{\Delta n}^{(d)}=\int\prod_{k=1}^{\Delta n}d\omega_k\prod_{k=2}^{\Delta n+1}A_k\prod_{k=2}^{\Delta n+1}(\omega_k)^{(1-d/2)}I_{d/2}(\omega_k)\times\exp\left(-\sum_{n=2}^{\Delta n+1}A_n^2\omega_n^2-\omega_1^2\right)f_{(\Delta n+2)}^{(d)} \tag{153}$$

and we can perform the same series expansion as in Sec. IV on the function defined by

$$h_{(\Delta n+1)}^{(d)}=A_{(\Delta n+1)}\int d\omega_{\Delta n+1}(\omega_{\Delta n+1})^{(1-d/2)}I_{d/2}(\omega_{\Delta n+1})\times\exp(-A_{\Delta n+1}^2\omega_{\Delta n+1}^2)f_{(\Delta n+2)}^{(d)} \tag{154}$$

to obtain $G_{\Delta n}^{(d)}$.

The series expansion of $f_{(\Delta n+2)}^{(d)}$ gives for the last term of $h_{(\Delta n+1)}^{(d)}$

$$\left(\frac{1}{2}\right)^{d/2}\frac{1}{\Gamma([d+1]/2)\Gamma(1/2)}\times\int_{-1}^{1}(1-t_{\Delta n+1}^2)^{(d-1)/2}dt_{\Delta n+1}A_{\Delta n+1}^{2n_{N-\Delta n-2}+1}\times\int_{-\infty}^{+\infty}d\omega_{\Delta n+1}\omega_{\Delta n+1}^{2n_{N-\Delta n-2}+1}\exp(-A_{\Delta n+1}^2\omega_{\Delta n+1}^2+\omega_{\Delta n+1}t_{\Delta n+1}), \tag{155}$$

whose integration over $\omega_{\Delta n+1}$ gives, due to the fact that the integrand is odd,

$$W\sum_{k=n_{\Delta n+1}}^{\infty}\frac{1}{k!}\left(\frac{1}{4}\right)^k\left(\frac{1}{A_{\Delta n+1}^2}\right)^k\frac{(2k+1)!}{[2(k-n_{\Delta n+1})+1]!}\times\int_{-1}^{1}(1-t_{\Delta n+1}^2)^{(d-1)/2}t_{\Delta n+1}^{[2(k-n_{\Delta n+1})+1]}dt_{\Delta n+1}=0. \tag{156}$$

Thus

$$G_{\Delta n}^{(d)}=0 \tag{157}$$

and

$$\langle(\mathbf{R}_{(n,p)})^2\rangle=a^2(p-n). \tag{158}$$

The last equation gives $\nu=\frac{1}{2}$ which is the same value as that for the Gaussian polymer. For the same reasons as given in Sec. IV, a simple argument could not give this result for any value of d because the analytical continuation to noninteger dimension is not always straightforward; the important point is to preserve something similar to the Euclidean scalar product. These results are given for any dimension d, but not for any space of dimension d because a regularity on the topological structure of the space is needed [20–22].

VII. CONCLUSION

We know that the Gaussian distribution for the end to end distribution of an ideal polymer is a consequence of the central limit theorem [1,6], and so this distribution is valid for $N\to\infty$; for finite values of N there are corrections in $1/N$ [6]. In the case of the FJC, the values of the critical exponents of ideal polymers have been recovered and, moreover, a very good approximation is given for its canonical partition function for almost all degrees of polymerization and for all physical dimensions of space $d\geqslant 2$, subject to topological regularity of the spaces with noninteger dimensions.

Thus, in principle, this ideal model of a polymer is completely solved. The analytical form of the partition function (107) is approximate for two reasons: (1) The multiplicative coefficients $A^{(d)}$ and $B^{(d)}$, coming from the metric determinant, are only approximated by hypergeometric functions; (2) the size of the box containing the polymer has been considered greater than the typical size of the polymer. For the latter approximation, an analytical study is difficult to make, while for the former, the coefficients $A^{(d)}$ and $B^{(d)}$ are computed from a straight line fit to the Monte Carlo data, and compared with the analytical approximation made with hypergeometric functions. The good agreement between the analytical and numerical results validates the analytical method used. For each dimension studied by means of the Monte Carlo integration, 498 points out of 499 are in agreement, with an accuracy of 1–3%, with the straight line fit. The Monte Carlo method has been applied for 28 values of the dimension of space between 2 and 8 (including noninteger dimensions). Thus for the 13 972 partition functions computed, 13 944 are in agreement with the partition function given by (107) with an accuracy of 1–3%. For each dimension studied, the only exception is for $N=3$. However, in that case the analytical form of the partition function is known exactly. In view of these results, Eq. (107) can be considered as nearly exact. The values of $A^{(d)}$ and $B^{(d)}$ given by the fit are all close to 1. $A^{(d)}$ is slightly bigger than 1 and $B^{(d)}$ is slightly smaller than 1 (see Table I). Both coefficients arise from the metric determinant of the FJC; thus we can conclude that the metric determinant produces only a weak perturbation of the value of the partition function [10]. This fact is known from numerical simulations where often the contribution from the frozen vibrational degree of freedom of the polyatomic molecules can be neglected [23,47]. The analytical method used to obtain the approximations allows one to describe the analogy between quantum mechanics and polymer physics via the Feynman formulation [46]. In the quantum theory of fields, the path formulation leads to the definition of the generating functional whose logarithmic derivatives with respect to the currents give the connected Green's functions [28]. In statistical physics, the partition function is similar to the generating functional. So, in polymer physics, it seems natural to use the Feynman formulation to compute the partition function rather than the Fokker-Planck equation. The use of Feynman rules allows us naturally to use conventional renormalization methods and so to find naturally a method similar to the decimation method [14,6]. The first stage of the conventional renormalization, applied to the FJC, gives an odd-even effect in the FJC. This effect has been observed by Fisher and Hiley [15] and by Grassberger and Hegger [16]. Because of the fractalization process explained in Sec. IV D and shown for one case in Fig. 2, one can suppose that FJC's whose degrees of polymerization belong to the same prefractal sequence have some common properties; this also leads one to suppose that other odd-even effects of higher order exist. The fractalization appears as the reverse of the decimation method; this might be easily tested because all analytical terms have finite values. The numerical estimate of the odd-even effect on the value of the coefficient $B^{(d)}$ in Eqs. (114) and (116) is given to first order in Sec. V C. In view of this effect the strange behavior of the FJC for $N=3$ is interpreted as a reminiscence of the odd-even effect. This effect appears to be smaller for the FJC than for realistic polymers models [16] and SAW's [15]; this certainly means that interaction between monomers amplifies this effect. With the knowledge of the partition function of the FJC made of N bonds, we can study all the equilibrium properties of the FJC. Thus we have recovered equipartition and found the Sakur-Tetrode relation for the FJC.

Considering the FJC as an ideal monatomic gas with the reduced phase space φ_{rest} it is possible to build the partition function of the FJC via Laplace transform in other thermodynamical ensembles. Thus, we have given the microcanonical partition function and the partition function of the grand canonical ensemble where the monomer number can fluctuate. In this grand canonical ensemble, a second chemical potential is associated with the number of bonds in the polymer. In the plane (χ,T) of this ensemble, we can define essentially two domains in which the system has very different behaviors: a monatomic domain where the average number of monomers in the FJC is less than 2, and in which the fluctuations of this number are quite small, and a polyatomic domain where the FJC is made of several monomers. In the monatomic domain the fluctuations of the average number of monomers in the FJC are small compared to the size of the system, whereas these fluctuations are of the same size as the system in the polyatomic domain. This domain is very strange and requires a careful study. First, this domain has a reentrant behavior with temperature (see Fig. 8) similar to the one occurring for the disordered phases in other systems [17–19]; this would lead one to define a double critical point and to consider that the second chemical potential is similar to a hydrogen bond strength [17]. The big fluctuations present in the domain do not allow one to consider it as a well defined phase. Because the fluctuations are of the same order of magnitude as the whole system, the polyatomic domain cannot be considered as a well defined phase. Nevertheless, the fluctuations always remain smaller than the system; thus the FJC is really polyatomic in this domain, but with a very high polydispersity.

In the grand canonical ensemble, there is a limiting value depending on the temperature for the second chemical potential, at which the system becomes infinite. This FJC of infinite length appears at high as well as low temperature for a positive second chemical potential. This phenomenon looks like the Bose condensation because the limit on the chemical potential is defined with the same criterion on geometrical series. It may be surprising to find that the reentrant infinite FJC has the same behavior at high and low temperatures (the critical exponent ν is independent of the temperature). This is, of course, a consequence of the fact that our system is classical. In recent work by Golubović and Xie [48], it has been shown that if one takes quantum fluctuations into account, one finds, for low temperatures and for a non-self-avoiding chain, a crumpled ground state having the appearance of a highly collapsed polymer with radius of gyration growing very slowly with N as $R\sim[\ln(N)]^{1/2}$ [48]. If we apply the FJC model to polyethylene with the same geometrical factors as in Ref. [48], we find using Eqs. (108) and (142) for $d=3$, $T_o(3)\approx1.516$ K, and

$$T_c=\frac{T_o}{2e}\simeq0.279\ \text{K},$$
$$\chi_c\simeq0.385\times10^{-23}\ \text{J}\simeq2.403\times10^{-5}\ \text{eV}. \tag{159}$$

T_c is not far from the Ginzburg temperature defined in [48]. The ''infinite real'' polymer in the low temperature limit would be in the crumpled ground state by a pure quantum effect, whereas our classical infinite FJC has the same behavior at low and high temperatures. Of course, in the case of these very low temperatures, our system (as well as the quantum system) is certainly meaningless because in the real world various things may happen, such as, for instance, crystallization, before reaching temperatures of the order of a few degrees kelvin. Even if one were able to experimentally cool an ideal polymer down to a few kelvins, in the crumpled ground state excluded volume effects cannot be neglected. Neither the FJC nor the ideal gas exists in the real world. They are very crude models of real systems. Moreover, it must be pointed out that the system studied in [48] is slightly different from a FJC since a harmonic potential between the bonds and a bending energy are used. Constant length for the bonds is not compatible with the uncertainty principle, unless the metric of the space is modified.

Throughout this work d is the dimension of the physical space and is taken as a real parameter greater than or equal to

2. The use of noninteger dimensions should be done with caution and if the results of the FJC are given for any dimension of space, they are not necessarily right for any space of dimension d. For example, the critical exponent ν must be defined in the fractal metric, otherwise an anomalous diffusion exponent θ appears that one may relate to the fractal dimension d_f by $\theta=2d_f-2$ [22]; thus in the fractal space one could recover $\nu=1/2$. But, even if we define ν with caution, internal to the fractal space, it may happen that the relationship between the fractal dimension and the anomalous diffusion exponent is not valid (for ramification orders greater than 1). The properties of the FJC in space with noninteger dimension depend on the topology of the space. Nevertheless, in a recent study by Bender and co-workers [20,21], ''random walks in noninteger dimension'' make sense, if we define rigorously the probabilities of walking outward or inward in some regions of the space [20]; otherwise, we may obtain unacceptable formulas for some probabilities (greater than 1 or less than 0). With their spherically symmetric random walks, they recover also the right Hausdorff dimension of a random walk [21]. Their construction is equivalent to a generalization of the Buffon needle construction (see note 7 of [20]). The FJC may be viewed as made of N Buffon needles, and one may use results of the FJC in noninteger dimension if we have shown previously that the topology of the noninteger space is correct for the FJC. The results of the FJC are not true for any fractal space. A criterion of validity might be the value of the critical exponent ν. Finally, Eqs. (144) give the connection with ideal polymers on regular lattices (i.e., random walks). In particular, Eqs. (144) give the coordination number of the equivalent lattice as a function of the temperature. Thus the FJC appears as a generalization of random walks on a lattice. Choosing a particular geometry for a regular lattice on which a random walk is performed is equivalent to choosing a temperature for the FJC model. To compare a random walk on a regular lattice with a given symmetry with another on a lattice of different symmetry but with the same lattice spacing and the same number of steps is equivalent to studying a FJC made of a number of bonds equal to the number of steps in the random walk and with a bond length equal to the lattice spacing at two different temperatures. For instance, in a two dimensional space, transferring a random walk from a triangular lattice $z_{\mathrm{tri}}=6$ to a square lattice $z_{\mathrm{squa}}=4$ is equivalent to cooling a FJC according to the rule

$$\left(\frac{T_{\mathrm{tri}}}{T_{\mathrm{squa}}}\right)^{(2-1)/2}=\frac{z_{\mathrm{tri}}}{z_{\mathrm{squa}}}=\frac{3}{2}. \tag{160}$$

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