Finite Size Distribution and Partition Functions of Gaussian Chains: Maximum Entropy Approach

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ABSTRACT: The distribution and partition functions of a Gaussian chain are calculated using the maximum entropy principle. The method allows the derivation of, analytically and in a simple manner, the distribution functions for chain molecules, taking into account various constraints for the chains itself as well as those formed by external restrictions. In particular the influence of different spatial constraints on the conformations of the chain is discussed. In the limit of an unrestricted chain the well-known Gaussian distribution function is reproduced. If the end points of the chain are subjected to various external constraints, novel results for the stress–strain relations for Gaussian chains are obtained. These relations especially describe the finite extensibility of a chain with a fixed number of segments. Furthermore, they are in qualitative agreement with known results on freely jointed chains of rigid rods.

I. Introduction

The most commonly used model of a polymeric chain in analytical theories is the Gaussian chain.[1-8] Although there exist further, more sophisticated models, the Gaussian chain is in most situations the only description of a polymer which can be manipulated analytically. Especially in renormalization group descriptions of polymer phenomena the Gaussian chain model is used, expressed mathematically in terms of Wiener integrals.[6-9] This representation is also applied in investigations of the influence of entanglements on molecular chains.[10,11]

The use of the Gaussian description is justified for several reasons. First of all, less convenient models provide the same macroscopic properties for a free chain in the limit of a large number of chain segments.[2,8] Moreover, the Gaussian chain is the minimal model that adequately describes several polymeric properties using the smallest number of phenomenological parameters. Since the microscopic statistical behavior of monomeric units cannot be taken into account in an analytical theory because of the complicated interactions of their constituents, the description by a Gaussian function at least reproduces their qualitative behavior. This holds for polymer properties, which involve length scales that are large compared to monomer sizes.

The distribution function of a chain molecule depends on its macroscopic constraints.[13] The usual description of a chain by Gaussian functions holds for a chain with a free end point. However, the result is also used in calculations of entropy elastic forces.[4] In this case, the resulting force extension relation does not reflect an essential property of a finite chain, namely, its finite extensibility. Therefore, we extend the existing description of Gaussian chains, taking into account their finite lengths. In order to achieve this goal, we calculate the distribution function of a chain under macroscopic constraints by the maximum entropy principle.[13] Depending on the constraints, the distribution function for macroscopic properties, like the end-to-end distance of a chain, is not necessarily given by the Gaussian function known from the literature.[1-4] Thus, we will denote a chain as Gaussian, if its distribution function on a microscopic scale is Gaussian, i.e., the distribution functions of the individual links of a chain are Gaussian. A similar microscopic description is used in the random-walk model of a chain.[6-9] Due to our generalized description of chain molecules we are able to calculate partition functions which depend on the macroscopic constraints and include the finite extensibility of the chains.

In section 2 we briefly summarize the maximum entropy principle and provide the fundamental formulas. Section 3 contains the application to chain molecules. The distribution function of a chain with a free end point is calculated. Then, the force extension relation of a chain with two fixed end points is investigated. Moreover, the partion function and the probability distribution of the end point for a chain are calculated, where only the mean position of this point is known. A similar calculation is performed for a chain with a given mean-square end-to-end distance. Finally, section 4 summarizes our findings.

II. Maximum Entropy Principle and Basic Equations

The maximum entropy principle (see, e.g., ref 14) allows the calculation of the equilibrium distribution function for a system of mass points under macroscopic constraints.[13] The basic quantity in this consideration is the entropy S defined by

$$S = -k_B \int \psi \ln \psi \, d^f q \, d^f p \tag{1}$$

where k_B denotes the Boltzmann constant, ψ is the distribution function, and $\{q\}$ and $\{p\}$ are the generalized coordinates and canonical conjugated momenta. The system of interest has f degrees of freedom. Since the entropy has an extremum in the equilibrium, the distribution function can be obtained by a variational calculation. Usually, the extremum has to be calculated under macroscopic constraints. One of the constraints is the normalization condition

$$\int \psi \, d^f q \, d^f p = 1 \tag{2}$$

Furthermore, we assume that the system of interest is constrained by expectation values ϕ_k of certain quantities $h_k(\{q\},\{p\})$, $k = 1, ..., M$:

$$\int \psi(\{q\},\{p\}) \, h_k(\{q\},\{p\}) \, d^f q \, d^f p = \phi_k \tag{3}$$

The ϕ_k's are given macroscopic quantities. To calculate the extremum of S in eq 1 with the constraints (2) and (3), as usual we use the method of Lagrangian multipliers. From the variation we obtain the following expression for

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the distribution function:

$$\psi = \frac{1}{Z}\exp(-\sum_{k=1}^{M}\lambda_k h_k) \tag{4}$$

Therefore the partition function is

$$Z = \int \exp(-\sum_{k=1}^{M}\lambda_k h_k)\, \mathrm{d}^f q\, \mathrm{d}^f p \tag{5}$$

It guarantees the normalization (2). The Lagrangian multipliers are obtained from the expectation values ϕ_k. From (3) we get

$$\phi_k = -\frac{\partial \ln Z}{\partial \lambda_k}, \quad k = 1, ..., M \tag{6}$$

These relations are in general a nonlinear system of equations from which the Lagrangian multipliers can be determined.

With (4) the maximum of the entropy (1) is given by

$$S = k_B(\ln Z + \sum_{k=1}^{M}\lambda_k \phi_k) \tag{7}$$

Additionally, we assume that the partition function depends on parameters α_i ($i = 1, ..., K$) such as the volume in which a system is confined; i.e., $Z = Z(\{\lambda\},\{\alpha\})$. These parameters take into account microscopic restrictions of the system, in contrast to the ϕ_i's, which represent macroscopic averages. Thus the independent parameters in S are the ϕ_i's and α_i's. In the variation of the entropy we consider Z to be an explicit function of the $\{\alpha\}$ and, via the λ_i, an implicit function of the α_i's and ϕ_i's. We then obtain for the variation of S

$$\delta S = k_B\left\{\sum_{k=1}^{K}\frac{\partial \ln Z}{\partial \alpha_k}\delta\alpha_k + \sum_{k=1}^{M}\lambda_k\, \delta\phi_k\right\} \tag{8}$$

In writing (8) the λ_k's and α_k's are considered to be independent variables. A similar calculation is given in ref 14 for a system assuming discrete states.

The advantage of the variational principle for the entropy is that only macroscopic expectation values and parameters are important. The microscopic interactions of the particles in the system do not have to be specified.

In the next section we will apply the above formulas to a model for a polymeric chain.

III. Gaussian Chain

We consider a one-dimensional arrangement of $N + 1$ mass points with equal masses m. The positions of the points are given by $\vec{r}_i$, $i = 0, ..., N$. Furthermore, it is assumed that the point $\vec{r}_0$ is fixed at the origin of the coordinate system. The other points are subjected to the constraints that the squared distances of successive points are constant in the ensemble average. Thus, we have to include the following geometrical constraints in the variation of the entropy

$$h_i = (\vec{r}_i - \vec{r}_{i-1})^2, \quad \phi_i = l^2, \quad i = 1, ..., N \tag{9}$$

In the subsequent sections, we will expose the end point $\vec{r}_N$ of the chain to various additional constraints. In addition, the mass points possess kinetic energy. Therefore, we have to take into account the constraint

$$h_{N+1} = H, \quad \phi_{N+1} = U \tag{10}$$

where H is the Hamiltonian of the system and U the macroscopic internal energy. At present we do not consider potential energy; therefore, the Hamiltonian contains only kinetic energy terms. However, the formalism is not restricted to this case; it is also possible to include potentials either by additional h's or directly in the Hamiltonian.

We will now discuss several additional constraints for the end point of the chain.

A. Gaussian Chain with a Free End Point. The simplest model which can be discussed by the given formalism is a chain with one free end; i.e., we consider a chain of N mobile points with $f = 3N$ degrees of freedom. Thus, we obtain the distribution function

$$\psi(\{x\},\{p\}) = \frac{1}{Z}\exp(-\sum_{i=1}^{N}\lambda_i(\vec{r}_i - \vec{r}_{i-1})^2)\exp(-\lambda_{N+1}H) \tag{11}$$

with

$$H = \sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m} \tag{12}$$

and the partition function

$$Z = \int \exp(-\sum_{i=1}^{N}\lambda_i(\vec{r}_i - \vec{r}_{i-1})^2)\exp(-\lambda_{N+1}H)\, \mathrm{d}^{3N}x\, \mathrm{d}^{3N}p \tag{13}$$

The partition function is straightforwardly calculated, and we obtain

$$Z = \pi^{3N}\left(\frac{2}{\lambda_{N+1}}\right)^{3N/2}\prod_{i=1}^{N}\left(\frac{m}{\lambda_i}\right)^{3/2} \tag{14}$$

Equation 6 yields the following equations for the calculation of the Lagrangian multipliers:

$$l^2 = 3/2\lambda_i, \; i = 1, ..., N \tag{15}$$

$$U = \frac{3N}{2\lambda_{N+1}} \tag{16}$$

The Lagrangian multipliers for the constrained distances are independent of each other and given by

$$\lambda_i = 3/2l^2 \tag{17}$$

From thermodynamics[15] we have $\partial U/\partial S = T$, and therefore, using (8), λ_{N+1} can be related to the temperature (T) of the system

$$\lambda_{N+1} = \frac{1}{k_B T} = \beta \tag{18}$$

Hence, the relation (16) yields the well-known result $U = (3/2)Nk_BT$ for the internal energy of the system. Finally, the distribution function is given by

$$\psi(\{x\},\{p\}) = \frac{1}{Z}\exp(-\beta H)\exp\left(-\frac{3}{2l^2}\sum_{i=1}^{N}(\vec{r}_i - \vec{r}_{i-1})^2\right) \tag{19}$$

Integration over the momenta and using (14)–(18) result in

$$\psi(\{x\}) = \left(\frac{3}{2\pi l^2}\right)^{3N/2}\exp\left(-\frac{3}{2l^2}\sum_{i=1}^{N}(\vec{r}_i - \vec{r}_{i-1})^2\right) \tag{20}$$

Consequently, the distribution function ψ is a product of independent Gaussian functions for the individual bonds. A chain like this is usually denoted as Gaussian.[7-9] Since the individual distances along the chain are distributed according to Gaussian standards, the distribution function

of the end point $\vec{r}_N$ is also Gaussian[2,3]

$$\psi(\vec{r}_N) = \left(\frac{3}{2\pi lL}\right)^{3/2} \exp\left(-\frac{3}{2lL}\vec{r}_N^{\,2}\right) \tag{21}$$

where $L = Nl$ is the total length of the chain. This can immediately be verified by integrating over all variables $\vec{r}_i$ ($i = 1, .., N-1$). From (8) we find that the entropy change for a system of constant internal energy, i.e., temperature, and constant segment length is zero. Consequently, it is impossible to calculate a force extension relation for this chain. In the literature (see, e.g., ref 2) frequently the relation $S = k_B \ln \psi(\vec{r}_N)$ is used to calculate the force extension relation. However, the considerations in section 2 show that this relation does not hold in general. The violation of the relation for the present system is not surprising. In order to change the end-to-end distance of the chain, one has to act on the end point. However, this is only possible if the end point of the chain is externally constrained. In this sense the end point of the above chain is free. In the following sections we investigate the influence of various constraints for the end point on the force extension relation of the chain.

B. Gaussian Chain with Two Fixed End Points. We now consider a chain where both end points are fixed ($\vec{r}_0 = 0, \vec{r}_N = \vec{a}$). In contrast to the previous calculations the number of degrees of freedom is therefore reduced to $f = 3(N-1)$. Similar to the chain with the free end, the distribution function expressed by the Lagrangian multipliers is given by (11). However, H has to be replaced by $H = \sum_{i=1}^{N-1}\vec{p}_i^{\,2}/2m$, and the partition function reads

$$Z = \int \exp(-\sum_{i=1}^{N}\lambda_i(\vec{r}_i - \vec{r}_{i-1})^2) \exp(-\beta H)\, \mathrm{d}^{3(N-1)}x\, \mathrm{d}^{3(N-1)}p \tag{22}$$

where $\vec{r}_N = \vec{a}$. Since the coordinates and momenta are decoupled, the Lagrangian multiplier λ_{N+1} is again equal to β (eq 18), and hence the total internal energy of the system is given by $U = (3/2)(N-1)k_BT$. For the calculation of the partition function we introduce the δ-function $\delta(\vec{r}_N - \vec{a})$ in (22) and integrate over $3N$ variables.

$$Z = C(T)\int \exp(-\sum_{i=1}^{N}\lambda_i(\vec{r}_i - \vec{r}_{i-1})^2)\, \delta(\vec{r}_N - \vec{a})\, \mathrm{d}^{3N}x \tag{23}$$

The temperature-dependent function $C(T) = (2\pi m k_B T)^{3(N-1)/2}$ stems from the integration over the momenta. By introducing difference vectors and using the Fourier representation of the δ-function, Z can be calculated in a straightforward manner. We finally find

$$Z = C(T)\pi^{3(N-1)/2}\left(\prod_{i=1}^{N}\lambda_i^{-3/2}\right)\left(\sum_{i=1}^{N}\frac{1}{\lambda_i}\right)^{-3/2} \exp\left(-\vec{a}^2\left(\sum_{i=1}^{N}\frac{1}{\lambda_i}\right)^{-1}\right) \tag{24}$$

Using relation (6), the Lagrangian multipliers have to be determined from

$$l^2 = \frac{3}{2\lambda_i} - \frac{3}{2\lambda_i^2}\left(\sum_{j=1}^{N}\frac{1}{\lambda_j}\right)^{-1} + \frac{\vec{a}^2}{\lambda_i^2}\left(\sum_{j=1}^{N}\frac{1}{\lambda_j}\right)^{-2}, \quad i = 1, ..., N \tag{25}$$

Equation (25) is a set of nonlinear equations. A solution is obtained by assuming equal Lagrangian multipliers ($\lambda_i = \lambda_j \; \forall \; i, j$). Physically this means that all segments along the chain are considered identical. We did not look for other solutions; therefore, we do not know whether there exist additional physical solutions of the equations. However, from a physical point of view, we believe that a different behavior of the segments can only be expected from segments close to the chain ends. Consequently, the Lagrangian multipliers are equal for the rest of the chain. In this case we obtain

$$\lambda_i = \frac{3}{2}\frac{N(N-1)}{L^2 - \vec{a}^2} \tag{26}$$

where L is again the total length of the chain. The expression exhibits a strong dependence of the Lagrangian multipliers on the end-to-end distance of the chain. In the limit $|\vec{a}| \to L$ the λ_i's become infinite. It is important to note that, due to the dependence of the Lagrangian multiplier on $\vec{a}$, the distribution function $\psi\{x\}$ is no longer equivalent to a random-walk distribution function. The introduction of additional microscopic or macroscopic constraints, aside from the conditions given in (9), destroys the independence of the individual points along the chain. For the current chain, the behavior of the points along the chain depends on the position of the end point. With (26), the partition function (24) reads

$$Z = C(T)\, N^{-3/2}\left(\frac{2\pi}{3N(N-1)}\right)^{3(N-1)/2}(L^2 - a^2)^{3(N-1)/2} \exp\left(-\frac{3}{2}\frac{(N-1)a^2}{L^2 - a^2}\right) \tag{27}$$

Z depends in a complicated manner on the end-to-end distance $\vec{a}$. In the limit $a \to L$ the partition function decreases to zero.

Since the end point of the chain is fixed, its position is always exactly known and its distribution function a δ-function. Consequently, the relation $S = k_B \ln \psi(\vec{a})$ cannot be used to calculate the entropy.

The change in entropy with the variation of the end-to-end distance is given by (8).

$$\delta S = k_B \nabla_a \ln Z\, \delta\vec{a} \tag{28}$$

The gradient ∇_a denotes the derivative with respect to $\vec{a}$. By using the partition function (27), we find

$$\delta S = -\frac{3(N-1)k_B}{L^2 - a^2}\vec{a}\, \delta\vec{a} \tag{29}$$

(Note that, according to the discussion in connection with (8), in (28) we have to use Z from (24), with the λ_i's not yet inserted, and not the partition function (27).) Because of the product $\vec{a}\, \delta\vec{a}$ a change in entropy is only obtained if the distance a is changed. A pure rotation does not yield a change in entropy. A connection between the change in entropy and the external force $\vec{F}$ necessary to stretch the chain is established by thermodynamics. For a chain with deformation-independent internal energy and purely deformational work, the force is given by[4]

$$\vec{F} = -T\nabla_a S \tag{30}$$

Hence, we obtain

$$\vec{F} = 3(N-1)k_BT\frac{\vec{a}}{L^2 - a^2} \tag{31}$$

As a result, we find a nonlinear force extension relation, where the force is directed along the distance vector $\vec{a}$. In the limit of a small end-to-end distance $a \ll L$ ($L^2 - a^2 \approx L^2$) and large N ($N \gg 1$) the force is given by

$$F \approx \frac{3k_BT}{l}\frac{a}{L} \tag{32}$$

This relation is usually obtained for Gaussian chains.[1,2,4]

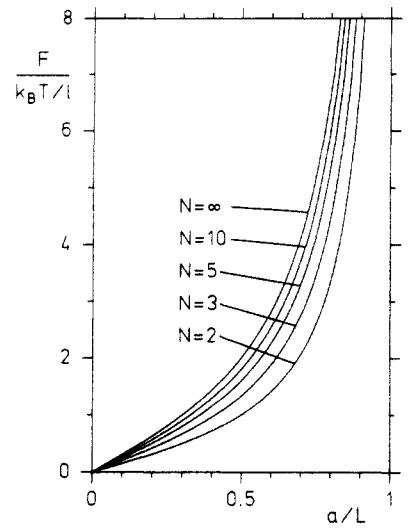

Figure 1. Force extension relations for Gaussian chains with different numbers of segments (N) and fixed end points.

For end-to-end distances comparable with the total length of the chain the force can be written as

$$F \approx \frac{3k_BT}{2l}\frac{a}{L-a} \tag{33}$$

Consequently, the force becomes infinite for $a \to L$; i.e., we have a chain with finite extensibility. In phenomenological descriptions of the stress–strain behavior of polymeric networks a similar singularity is assumed.[12]

Figure 1 shows the normalized force as a function of the reduced extension a/L and the number (N) of segments of the chain. The figure exhibits the linear increase of the force for small extensions and the singularity as a approaches the length of the chain. According to (31), the force at a given distance a increases with increasing N. For $N \to \infty$ (L fixed) a limiting curve is approached.

The variational concept of the entropy provides a nonlinear force extension relation which agrees qualitatively with the results of more complicated theories:[2,16,17] For small end-to-end distances the force increases linearly and exhibits a singularity for $a \to L$. To our knowledge a relation similar to that in (31) was never obtained analytically before. In refs 18 and 19 the force (31) in the limit $N \to \infty$ was used as an empirical simplification of more complicated force extension relations.

C. Gaussian Chain with a Given Mean End-to-End Distance. So far we discussed the behavior of chains with one free end point (section A) and both end points fixed (section B). We now address the problem of chains in which one end point is allowed to fluctuate about a given value. This is achieved by introducing the constraint

$$\langle \vec{r}_N \rangle = \vec{a} \tag{34}$$

for the end point $\vec{r}_N$ of the chain. The brackets $\langle ... \rangle$ denote the average using an appropriate distribution function, which has to be determined. Since the restriction (34) allows fluctuations of the point N, the number of degrees of freedom is again $f = 3N$. Thus, similar to section 3.1 we obtain for the internal energy $U = (3/2)Nk_BT$. The partition function (5) reads

$$Z = C(T)\int \exp(-\sum_{i=1}^{N}\lambda_i(\vec{r}_i - \vec{r}_{i-1})^2)\exp(-\vec{\lambda}\vec{r}_N)\,\mathrm{d}^{3N}x \tag{35}$$

where $C(T) = (2\pi mk_BT)^{3N/2}$ is again the contribution of the momenta and the constraints (9), (10), and (34) are taken into account. The relation (34) represents three constraints. For notational convenience, we collected the corresponding Lagrangian parameters in the vector $\vec{\lambda}$. By introducing difference vectors, the integrals in Z can be evaluated. We finally arrive at the following expression:

$$Z = C(T)\prod_{i=1}^{N}\left(\frac{\pi}{\lambda_i}\right)^{3/2}\exp\left(\frac{\vec{\lambda}^2}{4\lambda_i}\right) \tag{36}$$

The determining equations for the Lagrangian multipliers are given by (6).

$$l^2 = \frac{3}{2\lambda_i} + \frac{\vec{\lambda}^2}{4\lambda_i^2}, \quad i = 1, ..., N \tag{37}$$

$$\vec{a} = -\sum_{i=1}^{N}\frac{\vec{\lambda}}{2\lambda_i} \tag{38}$$

Elimination of $\vec{\lambda}$ yields

$$l^2 = \frac{3}{2\lambda_i} + \frac{\vec{a}^2}{\lambda_i^2}\left(\sum_{j=1}^{N}\frac{1}{\lambda_j}\right)^{-2}, \quad i = 1, ..., N \tag{39}$$

Thus, we obtain a nonlinear set of equations to determine the Lagrangian multipliers of connectivity. The assumption of equal multipliers yields

$$\lambda_i = \frac{3}{2}\frac{N^2}{L^2 - \vec{a}^2}, \quad \forall i \tag{40}$$

and

$$\vec{\lambda} = -3N\frac{\vec{a}}{L^2 - \vec{a}^2} \tag{41}$$

Finally, the partition function reads

$$Z = C(T)\left(\frac{2\pi}{3N^2}\right)^{3N/2}(L^2 - a^2)^{3N/2}\exp\left(\frac{3}{2}\frac{Na^2}{L^2 - a^2}\right) \tag{42}$$

This partition function is significantly different from the one for a chain with fixed end points (eq 27). The partition function (27) decreases to zero in the limit $a \to L$. However, Z of (42) increases to infinity because of the different sign in the exponential function. The force extension relation is not affected by the difference, since this relation has to be determined in a different way. By changing the mean position $\vec{a}$ (8), the entropy changes according to

$$\delta S = k_B\vec{\lambda}\,\delta\vec{a} = -\frac{3Nk_B}{L^2 - a^2}\vec{a}\,\delta\vec{a} \tag{43}$$

Together with (30) we end up with the following force extension relation:

$$\vec{F} = 3Nk_BT\frac{\vec{a}}{L^2 - a^2} \tag{44}$$

Thus, apart from the factor N, we obtain the same force extension relation as for the chain with two fixed end points. Equation 44 is given by the limiting curve ($N = \infty$) in Figure 1. Comparison of (44) with (43) exhibits the physical meaning of the Lagrangian multiplier $\vec{\lambda}$. It is equal to the external force divided by k_BT. Ensembles which allow the end point to fluctuate while the external force is given are called *stress ensembles*, whereas ensembles of chains with fixed end points are denoted as *strain ensembles*.[20]

In order to investigate the fluctuations of the end point, we evaluate the distribution function for $\vec{r}_N$. The fun-

damental relation (4) yields

$$\psi(\vec{r}_N) = \left(\frac{3N}{2\pi(L^2 - \tilde{a}^2)}\right)^{3/2} \exp\left(-\frac{3N}{2}\frac{(\vec{r}_N - \tilde{a})^2}{L^2 - a^2}\right) \quad (45)$$

where we integrated over all intermediate points and used the relations (40) and (41). As shown by (45), the end point of the chain is fluctuating symmetrically about the mean position $\tilde{a}$ with a Gaussian distribution function. The width of the distribution function depends on the number of segments of the chain and the distance a. In the limit $a \to L$, $\psi(\vec{r}_N)$ becomes a δ-function; i.e., the position of the end point is exactly fixed in this limit. If $\tilde{a}$ is set equal to zero, the distribution function of the free chain (21) is obtained.

These findings can be underlined by calculating the mean-square end-to-end distance of a chain. The distribution function (45) yields

$$\langle \vec{r}_N{}^2 \rangle = a^2 + \frac{L^2 - a^2}{N} \quad (46)$$

For $\tilde{a} = 0$ the result of the free chain is obtained as $\langle \vec{r}_N{}^2 \rangle = lL$.[2,3,7] For $a = L$, the mean-square end-to-end distance is given by $\langle \vec{r}_N{}^2 \rangle = a^2$, indicating the exact determination of the position of the end point.

The difference between the force extension relation of a chain with fixed end points and a chain where only the mean position of the end point is given is small. They are only different in the number of degrees of freedom; i.e., $N - 1$ or N appears in the expression for the force. The maximum extension of the chains is not affected. In the limit of a large number of degrees of freedom, the difference can be neglected in the calculation of the force.

D. Gaussian Chain with a Given Mean-Square End-to-End Distance. We finally investigate the behavior of a Gaussian chain with the constraint of a given mean-square end-to-end distance; i.e.

$$\langle \vec{r}_N{}^2 \rangle = \tilde{a}^2 \quad (47)$$

The partition function (5) including the conditions (9), (10), and (47) reads

$$Z = C(T)\pi^{3N/2} \left(\prod_{i=1}^{N} \lambda_i^{-3/2}\right)\left(1 + \lambda_{N+1}\sum_{i=1}^{N}\frac{1}{\lambda_i}\right)^{-3/2} \quad (48)$$

The Lagrangian multipliers follow from the equations

$$l^2 = \frac{3}{2\lambda_i} - \frac{3\lambda_{N+1}}{2\lambda_i^2}\left(1 + \lambda_{N+1}\sum_{j=1}^{N}\frac{1}{\lambda_j}\right)^{-1}, \quad i = 1, ..., N \quad (49)$$

$$a^2 = \frac{3}{2}\left(\sum_{i=1}^{N}\frac{1}{\lambda_i}\right)\left(1 + \lambda_{N+1}\sum_{i=1}^{N}\frac{1}{\lambda_i}\right)^{-1} \quad (50)$$

By assuming again identical multipliers λ_i, the solution of the above set of equations is given by

$$\lambda_i = \frac{3N(N-1)}{2(L^2 - a^2)} \quad (51)$$

$$\lambda_{N+1} = \frac{3}{2a^2} - \frac{3(N-1)}{2(L^2 - a^2)} \quad (52)$$

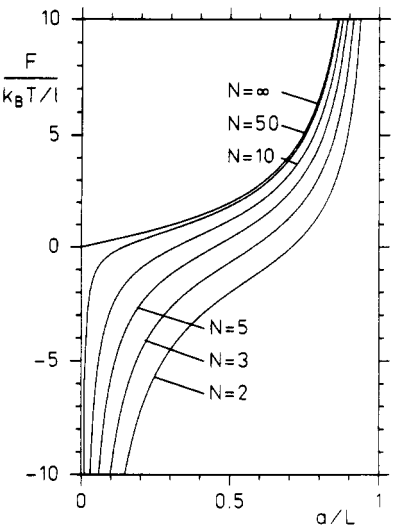

Figure 2. Force extension relations for Gaussian chains with different numbers of segments (N) and a given mean-square end-to-end distance.

Finally, the partition function reads

$$Z = C(T)\left(\frac{2\pi(L^2 - a^2)}{3N(N-1)}\right)^{3(N-1)/2}\left(\frac{2\pi a^2}{3N}\right)^{3/2} \quad (53)$$

From (8) we obtain the following change in entropy with varying $\tilde{a}$:

$$\delta S = k_B\left(\frac{3}{2a^2} - \frac{3(N-1)}{2(L^2 - a^2)}\right)\delta\tilde{a}^2 = 3k_B\left(\frac{1}{a^2} - \frac{N-1}{L^2 - a^2}\right)\tilde{a}\,\delta\tilde{a} \quad (54)$$

Thus, the force is given by

$$\vec{F} = 3k_B T\left(\frac{N-1}{L^2 - a^2} - \frac{1}{a^2}\right)\tilde{a} \quad (55)$$

As compared to the force extension relations (31) and (44), (55) contains an additional term $-a^{-2}$. Hence, the force no longer vanishes at $a = 0$, but rather at $a_0^2 = Nl^2$. For extensions smaller than a_0 the force F is negative (cf. Figure 2); i.e., the end points of the chain have to be pressed together in order to shorten the end-to-end distance.

The force extension relation (55) is shown in Figure 2, again in scaled units. The figure shows the decrease of the force to minus infinity for $a \to 0$. At the maximum extension $a = L$ the force is again infinite. In between the force exhibits a change in sign at $a = a_0$. The value $a_0/N \propto N^{-1/2}$ for which the force is zero is shifted toward zero with increasing number of segments N (cf. Figure 2). In the limit of an infinite number of segments, (55) agrees with the force derived for a chain with fixed end points and for a chain with a given mean end-to-end distance, respectively.

Further differences to the chain with a given mean end-to-end distance can be discussed with the help of the distribution function of the end point. The general expression (4) together with the partition function (53) and the Lagrangian multipliers (51) and (52) yields the following distribution function of the end point:

$$\psi(\vec{r}_N) = \left(\frac{3}{2\pi a^2}\right)^{3/2} \exp\left(-\frac{3\vec{r}_N{}^2}{2a^2}\right) \quad (56)$$

The distribution function is a Gaussian with mean $\langle \vec{r}_N \rangle = 0$. The width of the distribution is equal to the given distance a. If a is replaced by the equilibrium distance a_0, we obtain the result of the free chain (eq 21). The distribution function for the chain with the constraint of a given mean end-to-end distance yields the same result

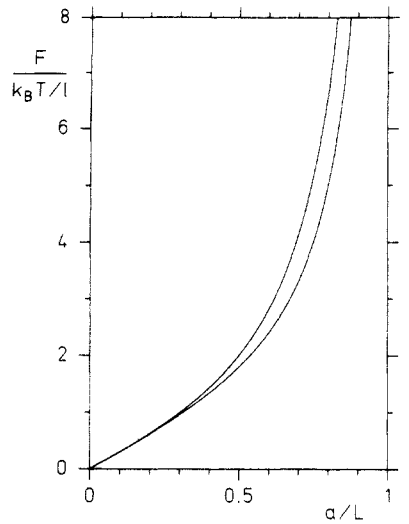

Figure 3. Comparison of the force extension relation of a Gaussian chain of a given mean end-to-end distance with a freely jointed chain. Upper curve: result of the Gaussian chain. Lower curve: inverse Langevin function.

for $\tilde{a} = 0$. For $\tilde{a}$'s larger than zero in (45), the distribution functions (45) and (56) reflect the different constraints. For a given mean-square end-to-end distance the mean position of the end point is always zero. This is a consequence of the fact that only the modulus of the distance is given. The point $\tilde{r}_N$ is free to fluctuate in a spherically symmetric manner about the point $\tilde{r}_0 = 0$. However, the end point of a chain with a given mean end-to-end distance is only allowed to fluctuate about $\tilde{a}$. These different possibilities of motion are reflected in the force extension relation.

Finally, Figure 3 compares the forces for a chain of a given mean end-to-end distance (eq 44) with the inverse Langevin function. This force is obtained in the limit of a large number of segments on the basis of a freely jointed chain.[2,3,13,16,17] The figure shows agreement between the forces at small end-to-end distances. With increasing separation of the end points, the force calculated by the variational method increases stronger than the inverse Langevin function. However, the qualitative behavior of the two models is the same.

IV. Conclusions

In the present paper we applied the maximum entropy principle to polymeric chains. We considered the chain as a one-dimensional arrangement of mass points. Without specifying the microscopic origin for the connectivity of the chain, we assumed the mean-square distances between successive points along the chain to be constant. In addition, one end point was fixed in space and the second one was subjected to various external constraints. In detail we considered the following cases: one fixed and one one free end point, two fixed end points, a chain with a given mean position of the second end point, and a chain with a given mean-square end-to-end distance. With the help of the maximum entropy principle we were able to calculate novel distribution and partition functions for the mass points along the chain depending on the constraints mentioned above. Furthermore, we calculated the force extension relation for these situations. For the chain with a free end point we reproduced the well-known end-point distribution function for a Gaussian chain. In contrast to the results in the literature,[2,4] we showed that a force extension relation cannot be calculated in this case. Our general formalism shows that a free chain cannot be stretched, because its stretching implies an external interaction. However, such an interaction can be produced by constraints. Accordingly, we calculated force extension relations for the chains with constrained end points as discussed above. All these relations reflect the finite extensibility of finite chains by the force increasing to infinity when the end-to-end distance of the chain approaches its contour length. Thus, our approach reproduces a result usually obtained only by more sophisticated models,[2,3,4,16] although we are just considering Gaussian chains. Furthermore, for a chain with a given mean-square end-to-end distance we obtain a finite equilibrium end-to-end distance (a_0). For extensions smaller than the equilibrium value the forces are negative; i.e., the chain ends have to be compressed to reduce the end-to-end distance. If the number of segments approaches infinity, the relative distance a_0/L decreases to zero.

Similar results were never obtained before on the basis of Gaussian phantom chains. As a consequence of the Gaussian description of the segments, our analytical expressions are much easier to manipulate than similar expressions of other models.

In summary, the method allows the calculation of certain macroscopic properties based on microscopic degrees of freedom without knowing there exact interrelations. In addition to the problems discussed above, we successfully applied the formalism to chains confined in a harmonic potential or a box. In each case results were found which improve the known ones. We also found new results for stiff Gaussian chains.[21] The variational approach was also applied to the statistics of polymer networks and provided, aside from novel results, a deeper understanding of the physics of networks.[22]

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