On a Wiener integral for an exact Kratky-Porod end to end distance

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Abstract. It is shown that a Chandrasekhar chain has associated a Wiener measure with a particular coupling between extensibility and curvature. Furthermore, a model with a general coupling parameter is discussed and it is shown that any other coupling different from that of Chandrasekhar chain, under the condition of average inextensibility, cannot either have a Kratky-Porod end to end distance nor the correct flexible limit

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1. Introduction

There are some problems in polymer physics where the stiffness of a chain plays an important role. For instance, in the statistics of entangled polymer, the curvature of the chain represents an upper bound to the "degree of entanglement", and therefore would be highly desirable to included stiffness in some theories which only characterize entanglements by lower bounds [1]. There has been a vast literature related to the statistics of stiff chains after the classical papers of Kratky and Porod [2], Hermans and Ullman and Daniels [4], most of it concentrated in the introduction of new mathematical techniques to solve the same problem or study specific asymptotic limits such as the rod limit. Whitin these techniques, functional integration has a special place since it provides a method for posing polymer problems with local or global constraints, such as stiffness or knots respectively.

Saito Takahashi and Yunoki [5] were the first to introduce functional integrals in the discussion of the statistics of stiff chains. They discussed models of stiff chains with constant or variable length, and gave a expression for their distribution function in terms of an infinite series of spherical harmonics and Hermite polynomials; they also calculated the first moments for such models and proposed a general method to calculate any moment (away from the rod limit) by expanding the characteristic function of the problem in terms of powers of k (k is the difference between in and out coming wave vectors). The latter method was developed explicitly by Yamakawa, obtaining expressions for the distributions and moments of a stiff inextensible chain away from the rod limit. Furthermore, Yamakawa and Fuji [7] obtained, within the

WKB approximation, the distribution function and moments of a stiff inextensible chain near the rod limit. Although the work of all these authors is fairly comprehensive as far as statistics of stiff chains is concerned, their mathematical complexity inhibits their use in problems which are quite complex by themselves, such as topological constraints. The complexity of these theories arises from the introduction of the inextensibility condition which makes the choice of spherical polar coordinates unavoidable. There are other theories in which this conditions has been relaxed and imposed only in an average sense. In this category we find the work by Freed [8] and Tagami [9]. Freed [8] has discussed simple Wiener integrals for stiff chains which are exactly soluble in a closed form. However, as we shall see, this model does not have proper asymptotic limits, and furthermore we find some inconsistencies in the work by Freed. Tagami [9], on the other hand, proposed a model of a stiff chain which corresponded to an Ornstein Uhlenbeck process in the theory of Markoffian process, which we shall call from here on a "Chandrasekhar chain". This model has an exact Kratky-Porod end-to-end distance, proper asymptotic limits in all higher moments and mathematically speaking is very simple. Therefore, we found interesting to discuss Tagami's model in the light of functional integration.

In this paper we shall give a path integral representation for a "Chandrasekhar chain", and show that this model implies a particular coupling between extensibility and curvature of the chain. Furthermore, we generalize this model to other coupling constant.

2. The Wiener measure for a Chandrasekhar chain

A Chandrasekhar chain will be one whose distribution function satisfies the following differential equation

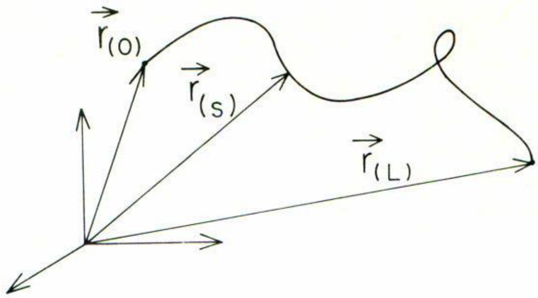
$$\frac{\partial G}{\partial L} + \nabla_{\mathbf{R}} \cdot (\mathbf{U}G) - \frac{\alpha}{\beta} U \cdot \nabla_{\mathbf{u}} G - \frac{1}{4\beta^2} \nabla_{\mathbf{u}}^2 G = \delta(L)\delta(\mathbf{R})\delta(U - U'), \tag{1}$$

together with the conditions

$$\langle U^2 \rangle = 1 \quad \text{(average inextensibility)} \tag{2}$$

and

$$P(U') = \frac{1}{4\pi}\delta(U'^2 - 1), \tag{3}$$



FIGUI

(first link random orientation and inextensibility) where

$$\mathbf{U} = \mathbf{u}(L) = \left.\frac{d\mathbf{r}(s)}{ds}\right|_{s=L}$$
$$\mathbf{U}' = \mathbf{u}(0) = \left.\frac{d\mathbf{r}(s)}{ds}\right|_{s=0} \tag{4}$$

$$\mathbf{R} = \mathbf{r}(L) - \mathbf{r}(0), \tag{5}$$

and $r(s)$ is the radius vector of monomer s being s the arch length along the chain as shown in Fig. 1.

In order to construct the Wiener measure associated to Eq. (1), we shall follow the method of convolution of "short length propagators" used by one of us (RAK) [10] some years ago. The method consists of constructing "short length Green's functions" from Eq. (1), and then, convolute them to obtain the full Green's function of Eq (1) in the form of a functional integral. The short length propagator of Eq. (1) for interval of length $\Delta_j S$, where $2 \leq j \leq M$, is

$$G(\Delta_j\mathbf{r}, \Delta_j\mathbf{u}, \Delta_j s) = k\delta\left(\frac{\mathbf{u}_j + \mathbf{u}_{j+2}}{2}\Delta_j s - \Delta_j\mathbf{r}\right) \times \exp\left\{-\beta^2\left(\frac{\Delta_j\mathbf{u}}{\Delta_j s} - \frac{\alpha}{\beta}\frac{\mathbf{u}_j + \mathbf{u}_{j+2}}{2}\right)^2 \Delta_j s\right\}, \tag{6}$$

where

$$\mathbf{u}_j = \mathbf{u}(s_j), \tag{7}$$

$$\Delta_j\mathbf{u} = \mathbf{u}(s_j) - \mathbf{u}(s_{j-2}), \tag{8}$$

$$\Delta_j \mathbf{r} = \mathbf{r}(s_j) - \mathbf{r}(s_{j-2}), \tag{9}$$

$$\Delta_j s = s_j - s_{j-2}, \tag{10}$$

and k is a function of $\Delta_j s$ only.

Convoluting, these short length propagators leaving fixed $\mathbf{r}(s_0) = 0$, $\mathbf{r}(s_M) = \mathbf{R}$, $\mathbf{u}(s_0) = \mathbf{U}'$ and $\mathbf{u}(s_M) = \mathbf{U}$, and taking the limit $M \to \infty$ (keeping the total length equal to L) we get the full Green's function of the Fokker-Planck equation

$$\begin{aligned} G(\mathbf{R}, \mathbf{U}\mathbf{U}', L) = & \lim_{\substack{M \to \infty \\ \sum_{j=1}^{M} \Delta_j s = L}} \mathcal{N} \int \cdots \int \prod_{j=0}^{M} d\mathbf{r}(s_j) \prod_{j=0}^{M} d\mathbf{u}(s_j) \\ & \times \delta(\mathbf{r}(s_0)) \delta(\mathbf{u}(s_0) - \mathbf{U}') \delta(\mathbf{r}(s_M) - \mathbf{R}) \delta(\mathbf{u}(s_M) - \mathbf{U}) \\ & \times \left\{ \prod_{j=2}^{M} \delta(\frac{u_j + u_{j-2}}{2} \Delta_j S - \Delta_j \mathbf{r}) \right. \\ & \left. \times \exp \left[-\beta^2 \sum_{j=2}^{M} \left[\frac{\Delta_j \mathbf{u}}{\Delta_j s} + \frac{\alpha}{\beta} \frac{u_j + u_{j-2}}{2} \right]^2 \Delta_j s \right] \right\}, \end{aligned} \tag{11}$$

where $s_0 = 0$, $s_M = L$ and $\mathcal{N}$ is a function of $\Delta_j s' s$ only.

In Gelfand's [11] notation of conditional Wiener integrals

$$\begin{aligned} G(\mathbf{R}, \mathbf{U}, \mathbf{U}', L) = \mathcal{N} \int_0^{\mathbf{R}} \int_{\mathbf{U}'}^{\mathbf{U}} \delta[r(s)] \delta[u(s)] \prod_s \delta(\mathbf{u}(s) ds - d\mathbf{r}(s)) \\ \times \exp \left\{ - \int_0^l \left[\beta \frac{d\mathbf{u}}{ds} + \alpha \mathbf{u} \right]^2 ds \right\}, \end{aligned} \tag{12}$$

or, alternatively, as

$$\begin{aligned} G(\mathbf{R}, \mathbf{U}, \mathbf{U}', L) = \mathcal{N} \int_{\mathbf{U}'}^{\mathbf{U}} \delta[u(s)] \delta \left(\mathbf{R} - \int_0^L \mathbf{u}(s) ds \right) \\ \times \exp \left\{ - \int_0^L \left[\alpha \mathbf{u} + \beta \frac{du}{ds} \right]^2 ds \right\} \end{aligned} \tag{13}$$

This means that a Chandrasekhar chain implies a particular coupling between length and curvature, that is $2\alpha\beta\mathbf{u} \cdot (d\mathbf{u}/ds)$.

The distribution function of the chain associated to this coupling, together with conditions (2) and (3), has been discussed thoroughly in Tagami's [9] paper. However, it is interesting to summarize the properties of this model. First, the relation imposed by conditions (2) and (3), between α and β, is *independent* of L, that is

$$\alpha\beta = \frac{3}{4}. \tag{14}$$

Secondly, the persistence length for this model is

$$\ell_p = \left\langle \frac{\mathbf{R}\cdot\mathbf{U}'}{|U'|} \right\rangle = \frac{\beta}{\alpha}\left(1 - e^{-\frac{\alpha}{\beta}L}\right). \tag{15}$$

Yet by definition

$$\ell_p = a\left(1 - e^{-L/a}\right). \tag{16}$$

Therefore the persistence lenght parameter a is *identical* to

$$a \equiv \frac{\beta}{\alpha} \tag{17}$$

Thirdly,

$$\langle R^2 \rangle = \frac{3L}{2\alpha^2} - \frac{3\beta}{2\alpha^3}\left[1 - e^{-\frac{\alpha}{\beta}L}\right], \tag{18}$$

which together with equations (14) and (17) can be written *exactly* as a Kratkly-Porod [2] end-to-end distance

$$\langle R^2 \rangle = 2aL - 2a^2\left(1 - e^{-L/a}\right). \tag{19}$$

And last but not least, all higher moments have proper asymptotic behaviour in the flexible as much as in the rod limit.

One now wonders if we could improve the performance of this model by changing the coupling constant. This we shall discuss in the next section.

3. A generalized model for a stiff chain

Let us now propose a model whose distributions function is generated by the Wiener mesure

$$\exp\left\{-\int_0^L (\alpha^2\mathbf{u}^2 + \beta^2\left(\frac{d\mathbf{u}}{ds}\right)^2 + 2\gamma\frac{d\mathbf{u}}{ds}\cdot\mathbf{u})ds\right\}, \tag{20}$$

where γ is now a general coupling parameter. At the same time we shall demand that the chain is *on the average* inextensible, that is,

$$\langle U^2 \rangle = 1. \tag{21}$$

The distribution function will be given, for this model, by the following path integral

$$\begin{aligned} G(\mathbf{R},\mathbf{U},\mathbf{U}',L) = \mathcal{N} \int_{\mathbf{U}'}^{\mathbf{U}} \delta[\mathbf{u}(s)] \delta \left(\mathbf{R} - \int_0^L \mathbf{u}(s) ds \right) \\ \times \exp \left\{ - \int_0^L \left(\alpha^2 u^2 + \beta^2 \left(\frac{du}{ds} \right)^2 + 2\gamma \frac{d\mathbf{u}}{ds} \cdot \mathbf{u} \right) ds \right\}, \end{aligned} \tag{22}$$

where the notation implies that $\mathbf{u}(0) = \mathbf{U}'$ and $\mathbf{u}(L) = \mathbf{U}$ and $\mathcal{N}$ is a normalizing constant whose value depends on whether G is a joint or a conditional probability function. When $\gamma = \alpha\beta$, G can *only* be a conditional probability function since if we integrate with respect to $\mathbf{R}$ and $\mathbf{U}$ we will get a constant independent of U' and therefore, we must multiply by a probability function of U' in order to obtain a joint probability function. That is not the case when $\gamma \neq \alpha\beta$ which has brought some confusion in the literature [8].

In order to give an explicit expression for $G(\mathbf{R},\mathbf{U},\mathbf{U}',L)$ we can proceed to find the corresponding differential equation and solve it, or else, to integrate directly the functional integral. We shall follow the latter procedure, since in the case of Gaussian functionals the problem can be solved exactly [12].

First of all, let us write G in the following way

$$G(\mathbf{R},\mathbf{U},\mathbf{U}',L) = \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k}\cdot\mathbf{R}} I(\mathbf{k},\mathbf{U},\mathbf{U}',L) d^3\mathbf{k}, \tag{23}$$

where

$$\begin{aligned} I(\mathbf{k},\mathbf{U},\mathbf{U}',L) = \mathcal{N} \int_{\mathbf{U}'}^{U} \delta[u(s)] \\ \times \exp \left\{ - \int_0^L \left(\alpha^2 \mathbf{u}^2 + \beta^2 \left(\frac{d\mathbf{u}}{ds} \right)^2 + 2\gamma \frac{d\mathbf{u}}{ds} \cdot \mathbf{u} - i\mathbf{k}\cdot\mathbf{u} \right) ds \right\}. \end{aligned} \tag{24}$$

The solution of (5) is given by [12]

$$I(\mathbf{k},\mathbf{U},\mathbf{U}',L) = F(L) e^{-S_{\text{clas}}(\mathbf{U}\mathbf{U}',L,k)}, \tag{25}$$

where $F(L)$ is an arbitrary function of L, which is fixed by normalization, S_{clas} is the first Hamilton integral calculated at the "classical path", that is,

$$S = \int_0^L \left(\alpha^2 u^2 + \beta^2 \left(\frac{d\mathbf{u}}{ds} \right)^2 + 2\gamma \frac{d\mathbf{u}}{ds} \cdot \mathbf{u} - i\mathbf{k} \cdot \mathbf{u} \right) ds, \tag{26}$$

and the classical path is the one for which

$$\delta S = 0. \tag{27}$$

Calculating S_{clas} we find

$$\begin{aligned} S_{\text{clas}}(U'U, L, k) = {} & \frac{\alpha\beta}{\operatorname{senh} \frac{\alpha}{\beta} L} \left[\cosh \frac{\alpha}{\beta} L (\mathbf{U}'^2 + \mathbf{U}^2) - 2\mathbf{U} \cdot \mathbf{U}' \right] + \gamma(\mathbf{U}^2 - \mathbf{U}'^2) \\ & + i\mathbf{k} \cdot \left(\frac{\beta}{\alpha} \frac{(1 - \cosh \frac{\alpha}{\beta} L)}{\operatorname{senh} \frac{\alpha}{\beta} L} (\mathbf{U}' + \mathbf{U}) \right) \\ & + \frac{k^2}{2\alpha^2} \frac{\beta}{\alpha} \frac{(1 - \cosh \frac{\alpha}{\beta} L)}{\operatorname{senh} \frac{\alpha}{\beta} L} + \frac{k^2}{4\alpha^2} L. \end{aligned} \tag{28}$$

Substituting (28) and (25) into (23) we get, after arranging terms conveniently,

$$\begin{aligned} G(\mathbf{R}, \mathbf{U}, \mathbf{U}', L) = \mathcal{N} \exp \Bigg\{ & -\eta_1 \left(\mathbf{U} - \frac{1}{\eta_1} (\eta_2 \mathbf{U}' - B\mathbf{R}) \right)^2 \\ & - \frac{\alpha^2 \xi_1}{2\eta_1 A} \left(R + A' \left(1 + \frac{\xi_2}{\xi_1} \right) \mathbf{U}' \right)^2 - \frac{\alpha^2\beta^2 - \gamma^2}{\xi_1} U'^2 \Bigg\}, \end{aligned} \tag{29}$$

where

$$\begin{aligned} A &= \frac{L}{2} + A', & \xi_1 &= \gamma + \alpha\beta \coth \frac{\alpha}{\beta} L, \\ \eta_1 &= \xi_1 + BA', & \xi_2 &= \alpha\beta \operatorname{csch} \frac{\alpha}{\beta} L, \\ \eta_2 &= \xi_2 - BA', & & \\ B &= \frac{\alpha^2 A'}{2A}, & A' &= -\frac{\beta}{\alpha} \tan h \frac{\alpha}{2\beta} L \end{aligned} \tag{30}$$

and

$$\mathcal{N} = \left(\frac{\alpha^2(\alpha^2\beta^2 - \gamma^2)}{2\pi^3 A} \right)^{3/2}, \qquad \forall \gamma \neq \alpha\beta. \tag{31}$$

With the condition that

$$\int d^3\mathbf{R} d^3U d^3U' G(\mathbf{R},\mathbf{U},\mathbf{U}',L) = 1. \tag{32}$$

If we now calculate $\langle R^2\rangle$ we get

$$\langle R^2\rangle = \frac{3\eta_1 A}{\alpha^2\xi_1} + \frac{3A'^2}{2\xi_1}(\xi_1+\xi_2)^2\frac{1}{\alpha^2\beta^2-\gamma^2} \tag{33}$$

Notice that when $\alpha\beta=\gamma$, $\langle R^2\rangle \to \infty$. The reason for this is that when $\alpha\beta=\gamma$, we cannot normalize G as (32), since once we have integrated U and R, there is nothing left to be integrated. This means that in the case $\alpha\beta=\gamma$, G can only be normalized with respect to all the paths in phase space starting at U' and going elsewhere, which implies that G, in this case, is a *conditional probability distribution* instead of a joint probability distribution as (29) together with (31). In order to have the case $\gamma=\alpha\beta$ as a particular case of our model, we must construct a conditional probability distribution for this model. We will look into that after we have discussed the present case.

If we now demand an average inextensibility, it must be satisfied that

$$\langle U'^2\rangle = \frac{3}{2}\frac{\xi_1}{\alpha^2\beta^2-\gamma^2} = 1 \tag{34}$$

and

$$\langle U^2\rangle = \frac{3}{2\xi_1} + \frac{\xi_2^2}{\xi_1^2}\langle U'^2\rangle = 1. \tag{35}$$

However (34) and (35) imply respectively that

$$\xi_1 = \frac{2}{3}(\alpha^2\beta^2-\gamma^2) \tag{34.a}$$

and

$$\xi_1 = \frac{2}{3}(\alpha^2\beta^2-\gamma^2) + 2\gamma. \tag{35.a}$$

γ must be equal to 0 in order for these to be compatible. Hence the *only* case consistent with average inextensibility is $\gamma=0$. This was precisely the case discussed by Freed [8], and Harris and Hearst [13].

Yet if $\gamma=0$, $\langle R^2\rangle$ will have the simple structure

$$\langle R^2\rangle = \frac{3L}{2\alpha^2}, \tag{36}$$

where α must be written in terms of the persistence length. If we do not impose the average inextensibility condition we would be left free to choose the value of α. Freed [8] chooses it to be equal to

$$\alpha^2 = \frac{3}{2\ell}, \tag{37}$$

where ℓ is the monomer length. Therefore he obtains that $\langle R^2 \rangle = L\ell$, which is the result for a flexible chain. From there he concluded that the average process used was not the correct one. He then proceeds to propose a new averaging procedure were $G(\mathbf{R}, \mathbf{U}, \mathbf{U}', L)$ is treated as a conditional probability function; this is mathematically wrong, since *it is a joint probability* function. His mistake was to prefix the value of α as we will show.

On the other hand, Harris and Hearst [13] fixed the value of α as

$$\alpha = \frac{3}{2\ell_{\text{ef}}}, \tag{38}$$

were the effective monomer length is chosed to be

$$\ell_{\text{ef}} = 2a - \frac{2a^2}{L}\left(1 - e^{-L/a}\right). \tag{39}$$

In that way they get the Kratky-Porod result. Yet this choice is inconsistent with the definition of persistence length together with an average inextensibility condition as we shall see.

The persistence length for our model, when $\gamma = 0$ will have the following form

$$l_p = \left\langle \frac{\mathbf{R}\cdot\mathbf{U}'}{|U'|} \right\rangle = \frac{\beta}{\alpha}\tanh\frac{\alpha}{\beta}L\langle |U'| \rangle. \tag{40}$$

In the case $\gamma = 0$ average inextensibility condition establishes the following relation between α and β

$$\alpha\beta = \frac{3}{2}\coth\frac{\alpha}{\beta}L \tag{41}$$

or

$$\alpha^2 = \frac{3}{2}\frac{\alpha}{\beta}\coth\frac{\alpha}{\beta}L, \tag{41.a}$$

and $\langle |U'| \rangle$ will take the following value

$$\langle |U'| \rangle = \left(\frac{8}{3\pi}\right)^{1/2} \tag{42}$$

Therefore

$$\ell_p = \left(\frac{8}{3\pi}\right)^{1/2} \frac{3}{2\alpha^2} = a\left(1 - e^{-L/a}\right). \tag{43}$$

Hence

$$\langle R^2 \rangle = \left(\frac{3\pi}{8}\right)^{1/2} La\left(1 - e^{-L/a}\right), \tag{44}$$

which is a different result from that of Freed and Harris and Hearst, yet this result is fully consistent with the definition of persistence length and the average inextensibility condition. We see then that this model *cannot* give a Kratky-Porod end-to-end distance (if we define consistently the persistence length), and neither has proper asymptotic limits.

We shall now discuss a model for which the probability distribution of the direction of the first link is given by (3). For that, let us construct the conditional probability $G(\mathbf{R}, \mathbf{U} \mid \mathbf{U}', L)$ that the end of the chain is at position $\mathbf{R}$ and with direction $\mathbf{U}$ when the initial link, is at the origin with a direction $\mathbf{U}' \cdot G(\mathbf{R}, \mathbf{U} \mid \mathbf{U}', L)$ will differ from $G(\mathbf{R}, \mathbf{U}, \mathbf{U}', L)$ by its normalization, that is, we will have the following normalizing condition

$$\int d^3R d^3U G(\mathbf{R}, \mathbf{U} \mid \mathbf{U}'; L) = 1 \tag{45}$$

instead of (32).

Hence

$$\begin{aligned} G(\mathbf{R}, \mathbf{U} \mid \mathbf{U}', L) = \left(\frac{\alpha^2 \xi_1}{2A\pi^2}\right)^{3/2} \exp\Bigg\{ -\eta_1 \left(\mathbf{U} - \frac{1}{\eta_1}(\eta_2 \mathbf{U}' - B\mathbf{R})\right)^2 \\ - \frac{\alpha \xi_1}{2A\eta_1}\left(\mathbf{R} + A'\left(1 + \frac{\xi_2}{\xi_1}\right)\mathbf{U}'\right)^2 \Bigg\}. \end{aligned} \tag{46}$$

This conditional distribution function reduces to that of "Chandrasekhar Chain" for $\gamma = \alpha\beta$, and therefore has the properties mentioned before once we have used (2) and (3). For a different value of γ we have

$$\ell_p = \left\langle \frac{\mathbf{R} \cdot \mathbf{U}'}{|U'|^{\cdot}} \right\rangle = -A'\left(1 + \frac{\xi_2}{\xi_1}\right)\langle |U'| \rangle. \tag{47}$$

But, as $P(\mathbf{U}') = \frac{1}{4\pi}\delta(U'^2 - 1)$, $\langle |U| \rangle = 1$, we have

$$\ell_p = -A'\left(1 + \frac{\xi_2}{\xi_1}\right) = a\left(1 - e^{-L/a}\right) \tag{48}$$

and

$$\langle R^2 \rangle = \frac{3\eta_1 A}{\alpha\xi_1} + A'^2\left(1 + \frac{\xi_2}{\xi_1}\right)^2. \tag{49}$$

The persistence length parameter a, and the parameters of the model, are related through Eq. (48). However if we now impose the average inextensibility condition

$$\langle U^2 \rangle = \frac{3}{2\xi_1} + \frac{\xi_2^2}{\xi_1^2} = 1, \tag{50}$$

we will get

$$\xi_1 = \frac{\gamma^2 - \alpha^2\beta^2}{2\gamma - \frac{3}{2}}, \tag{51}$$

or

$$\gamma = \left(\frac{3}{4} - \alpha\beta\coth\frac{\alpha}{\beta}L\right) + \sqrt{\alpha^2\beta^2\operatorname{csch}^2\frac{\alpha}{\beta}L + \frac{9}{16}}. \tag{52}$$

Substituting (52) into (48) we have

$$\ell_p = \left\langle \frac{\mathbf{R}\cdot\mathbf{U}'}{|U'|} \right\rangle = \frac{\beta}{\alpha}\tanh\frac{\alpha}{2\beta}L\left(\frac{\alpha\beta\operatorname{csch}\frac{\alpha}{\beta}L}{\frac{3}{4} + \sqrt{\alpha^2\beta^2\operatorname{csch}\frac{\alpha}{\beta}L + \frac{9}{16}}} + 1\right). \tag{53}$$

As one sees, the relation between a, α and β, is fairly complex and only in few cases this expression reduces considerably.

On the other hand,

$$\langle R^2 \rangle = \frac{3L}{2\alpha^2} - \frac{2\beta}{\alpha}\tanh\frac{\alpha}{2\beta}L\left(\frac{3}{2\alpha^2} - \ell_p\right), \tag{54}$$

where ℓ_p is given by (53).

In the case where $\gamma = \alpha\beta = 3/4$, $\langle R^2 \rangle$ takes the Kratky-Porod form and $a \equiv \beta/\alpha$ as pointed out in section 2.

We now wonder if there is another value of α and β for which one could reduce $\langle R^2 \rangle$ to its Kratky-Porod form. Yet if $\langle R^2 \rangle$ is of the Kratky-Porod form, then this would imply another relation between a, α and β; that is

$$\frac{3L}{2\alpha^2} + 2A'\left(\frac{3}{2\alpha^2} - \ell_p\right) = 2a(L - \ell_p), \tag{55}$$

and therefore

$$a = \frac{\frac{3}{4}\frac{L}{\alpha^2} + A'\left(\frac{3}{2\alpha^2} - \ell_p\right)}{(L - \ell_p)}. \tag{56}$$

If we substitute this value of a into $a(1 - e^{-L/a})$, we do not recover the expression for ℓ_p given by (53), and consequently, (56) *is not compatible* with (53). Hence we conclude that $\gamma = \alpha\beta = 3/4$ is the *only* value that gives the exact end to end distance consistently with the definition of the persistence length parameter and the average inextensibility condition.

Let us now study the asymptotic behaviour of this model. When $\beta \to \infty$ with L finite (rod limit) ℓ_p and R^2 behave respectively as

$$\lim_{\beta\to\infty} \ell_p = L, \tag{57}$$

$$\lim_{\beta\to\infty} \langle R^2 \rangle = L^2, \tag{58}$$

which imply that this model has the correct rod limit. In the flexible chain limit ($L \to \infty$ with α/β finite) we have the following behaviour

$$\lim_{L\gg 1} \ell_p = \frac{\beta}{\alpha} = a, \tag{59}$$

$$\lim_{L\gg 1} \langle R^2 \rangle = \frac{3L}{2\alpha^2}. \tag{60}$$

In order for $\langle R^2 \rangle$ to take the correct flexible limit, $3/2\alpha^2$ must converge, in this limit, to $2a$, which implies that

$$\lim_{L\to\infty} \alpha\beta = \frac{3}{4}. \tag{61}$$

This means that in order to obtain the correct flexible chain limit we must impose the condition that, in this limit, the relation between the parameters of the model should converge to the relation between them in a "Chandrasekhar chain". If we substitute (61) into (52) we get for γ that

$$\lim_{L\to\infty} \gamma = \frac{3}{4}. \tag{62}$$

In the case $\gamma = 0$ we will get for this model that

$$\ell_p = \frac{3}{2\alpha^2} \tag{63}$$

and that

$$\langle R^2 \rangle = L\ell_p = La\left(1 - e^{-L/a}\right). \tag{64}$$

We see, from the previous discussion, that this model would only have the correct rod limit since γ has been prefixed at a different value than 3/4. It is interesting to point out also that, even within this model the choice of α by Harris and Hearst and Freed is not the correct one.

We observe that the rod limit basically depends on the probability distribution of the direction of the first link. If we choose (3) we get the correct asymptotic behaviour in all its moments. However if we are only interested in a second moment, then we could use a probability distribution which only have $\langle U'^2 \rangle$ and $\langle |U'| \rangle$ equal to one, regardless of higher moments.

4. Conclusions

From the previous sections, we see that a different coupling between extensibility and curvature from that of a Chandrasekhar chain leads to complicated relations between its parameters without offering advantages. Even the uncoupled case $\gamma = 0$ has a more complicated relation between the parameters of the model, and does not have adequate asymptotic limits. Therefore, we would conclude that a Chandrasekhar chain is the simplest model which has the exact second moment and the correct asymptotic behaviour. Any other coupling will *neither have* a Kratky-Porod end-to-end distance nor the correct flexible limit unless we impose the condition that, in this limit, the parameters of the model are related as in a Chandrasekhar chain.

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Resumen. Se muestra que una cadena de Chandrasekhar tiene asociada una medida de Wiener con un acoplamiento particular entre la extensibilidad y la curvatura. Además, se discute un modelo con un parámetro de acoplamiento general, y se muestra que cualquier otro acoplamiento diferente del de la cadena de Chandrasekhar, bajo la condición de inextensibilidad promedio, no puede tener una distancia extremo-extremo de Kratky-Porod, ni tiene el límite flexible correcto.