On the Conformational Geometry for "almost" Self-Avoiding Polymers Chains

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Abstract

We deduce the effective ordinary non-linear differential equations satisfied by the moments associated to the end-to-end probability distribution of a polymer chain in the presence of a potential simulating phenomenologically the self-avoidance of the chain with the z-axis. Additionally, we show by a straightforward asymptotic analysis of a large number of links that the above cited chain distribution moments effective ordinary differential equations for such "almost" self-avoiding chain, reaches out further into the usual three-dimensional space than the usual gaussian chain.

Introduction

One of the most outstanding problem in the "Polymer physics" is to explain the feature of the geometrical (conformational) property related to the experimental fact that the self-avoiding Polymer chain reaches out into the usual space more than the usual gaussian one and described mathematically by a growing of the square moment distribution (in relation to the chain number of links N) of the following form $< \vec{r}^{\,2}(N) > \sim N^{\bar{\nu}}$ with $\bar{\nu} \sim 1 + \dfrac{1}{6} > 1$ ([1]).

We aim in this Brief Report to show such asymptotic growing by a simple and straight-forward analysis of a set of effective ordinary differential equations satisfied by the moment distributions associated to the above problem and proposed by us. In order to obtain this result we follow F.W. Wiegel ([2]) by substituting the delta-function interaction between the polymer chain monomer at a planar radial distance ρ with the z-axis by a potential of the form $V(\rho) = \dfrac{A}{\rho^2 + \delta^2}$ with a "hard-care" parameter δ very small in relation to the monomer lenght σ.

This Brief report is organized as follows:

In section 1 we deduce the set of effective ordinary differential-integral equations satisfied by the moment distributions associated to the end-to-end probability distribution of a polymer chain in thermal equilibrium with the "solvent-environment" and added with the presence of a general potential $V(\vec{r})$.

In section 2, we apply the results obtained in section 1 to the problem of "almost" self-avoidance with a linear ([3]) and moddeled by the above described phenomenological Wiegel potential.

1   The Moments Probability Distribution Equation

Let us start our analyse by considering the general partial differential diffusion equation governing the end-to-end polymer chain probability distribution $\rho(\vec{r}; N)$ in the presence of a potential of a force par monomer denoted by $V(r)$

$$\frac{\partial \rho(\vec{r}, N)}{\partial N} = \frac{\sigma^2}{6} \, \Delta \, \rho(\vec{r}, N) - \beta \, V(\vec{r}) \rho(\vec{r}, N) \tag{1}$$

with the initial condition

$$\rho(\vec{r}, 0) = \delta(\vec{r} - \vec{r}')$$

(2)

and prossesing the information where the polymer chain start its replication. Here σ is the monomer lenght forming the polymer chain.

It is a somewhat cumbersome problem of mathematical methods on Physics the search of exact solutions of eqs. (1)-(2). At this point we alternatively propose to consider directly the associated effective ordinary differential equations satisfied by the moments and the geometrical vector position of the polymer chain averaged with the probability chain density. Let us, thus, consider for simplicity of exposition the three basic objects to describe the conformational geometry of our polymer at large-order behavior for N. We have, thus, to consider the following objects: the polymer partition function

$$Z(N) = \int d^3\vec{r} \, \rho(\vec{r}; N)$$

(3)

the averaged chain vector position

$$\vec{R}(N) = \langle \vec{r} \rangle(N) = \left(\int d^3\vec{r} \, \rho(\vec{r}; N) \cdot \vec{r} \right) \Big/ Z(N)$$

(4)

and the chain giration radius

$$R^2(N) = \langle (\vec{r} \cdot \vec{r}) \rangle(N) = \left(\int d^3\vec{r} \, \rho(\vec{r}; N)(\vec{r})^2 \right) \Big/ Z(N)$$

(5)

It is straightforward, for instance, to show that $\vec{R}(N)$ satisfies the following relation after using the definition eq. (4) and eq. (1)

$$\frac{d}{dN}\vec{R}(N) = -\beta \left\{ \int_{-\infty}^{+\infty} d^3\vec{k} \, \tilde{V}(\vec{k}) \, \frac{1}{i} \nabla_{\vec{k}} \langle e^{i\vec{k}\cdot\vec{r}} \rangle \right\} - \frac{Z'(N)}{Z(N)} \vec{R}(N)$$

(6)

where $\tilde{V}(k)$ denotes the Fourier transform of the environment potential $V(\vec{r})$, and, of course, $\langle \, \rangle$ denotes the end-to-end probability distribution of our polymer chain eq. (1).

Let us firstly point out that under the leading approximation of the first order of the cummulant expansion of the Fourier transform Kernel (or equivalently for low conformational frequency region $|\vec{k}|^2 \simeq 0$)

$$\langle e^{i\vec{k}\cdot\vec{r}} \rangle = e^{i\vec{k}\cdot\langle\vec{r}\rangle}$$

(7)

the relation eq. (6) turns into the following first order ordinary non-linear differential equation for the chain vector position

$$\frac{d}{dN}\vec{R}(N) = -\beta \ \vec{R}(N) \times V(\vec{R}(N)) - \left(\frac{Z'(N)}{Z(N)}\vec{R}(N)\right) \tag{8}$$

By proceeding by the same steps exposed above, we obtain that at first order commulant approximation, the chain radius giration satisfies and *exactly* soluble first-order ordinary differential equation

$$\frac{d}{dN}(R^2(N)) = \sigma^2 - \beta(\vec{R}(N))^2 V(\vec{R}(N)) - \left(\frac{Z'(N)}{Z(N)}(R^2(N))\right) \tag{9}$$

At this point we remark the appearance of a damping term with a damping constant variable with the chain lenght N in eq. (8) and eq. (9).

The chain partition function $Z(N)$ will be taken to be known in our study from hereafter ([1], [2], [4]). However, its chain lenght evolution equation is easily written down

$$\frac{d}{dN}Z(N) = -\beta V(0)Z(N) - \beta(\vec{R}(N) \cdot \nabla \vec{v}(0)) + \cdots \tag{10}$$

where the terms in coma $\cdots$ have the meaning of involving higher-derivatives of the potential $V(\vec{r})$ at the origin and higher order moments.

Related to problem of taking higher order corrections in the cummulant expansion of the Fourier Kernel $exp(i\vec{k} \cdot \vec{r})$, let us show how to proceed in the case of second order corrections in our effective ordinary differential equations. We consider, thus, the corrected expansion

$$\langle e^{i\vec{k} \cdot \vec{r}} \rangle_{(N)} = e^{i\vec{k} \cdot \langle \vec{r} \rangle(N)} e^{-\frac{1}{2}\left\{|\vec{k}|^2(\langle(\vec{r})^2\rangle - \langle\vec{r}\rangle^2)(N)\right\}} \tag{11}$$

the relation eq. (6) takes the integro-differential form but involving now the giration radius in its functional structure and, thus, becoming a non closed integro-differential equation, opposite to eq. (8) in the first order approximation

$$\frac{d}{dN}\vec{R}(N) = -\left(\beta\vec{R}(N)\left\{\int d^3y \ V(\vec{y})G(\vec{R}, R^2, \vec{y})\right\}\right) - \left(\beta(R^2(N) - (\vec{R} \cdot \vec{R})(N))\right.$$
$$\nabla_{\vec{R}(N)}\left\{\int d^3y \ V(\vec{y})G(\vec{R}, R^2, \vec{y})\right\}\right) - \left(\left(\frac{Z'(N)}{Z(N)}\right)\vec{R}(N)\right) \tag{12}$$

where

$$G(\vec{R}, R^2, \vec{y}) = [R^2(N) - (\vec{R} \cdot \vec{R})(N)]^{-3/2} exp \left\{ -\frac{1}{2} \left[\frac{(\vec{R}(N) - \vec{y})^2}{(R^2(N) - (\vec{R} \cdot \vec{R})(N))} \right] \right\} \qquad (13)$$

Similar correction on the cummulant expansion for the Fourier-Kernel can be considered for the chain giration radius. Another point worth remark is the explicit solution of eq. (9) for the chain giration radius

$$R^2(N) = \frac{1}{Z(N)} \left\{ \int_0^N dN' \ Z(N') \left[(\sigma^2 - \beta(\vec{R}(N'))^2 V(\vec{R}(N'))) + 1 \right] \right\} \qquad (14)$$

Note that we have re-introduced the monomer lenght σ in eq. (9).

We now proceed to show that in these somewhat first order approximations an "almost" self-avoiding chain is "bigger" than the usual Free (Gaussian) polymer chain in the next section of our study.

2 The "Almost Self-Avoiding Case

In this section we apply the previous framework to analyze the Physico-Chemical importance case of a Polymer chain in a phenomenological interaction with the z-axis though the Wiegel potential with a "hard-core" parameter σ in the radial distance of the chains monomer to the z-axis with the following behaviour of the polymer chain partition functional for large number of links N

$$Z(N) \sim N^{-\gamma} \qquad (15)$$

with the positive exponent γ equals to $\gamma = 2 - \varepsilon$ where $\varepsilon \sim 1/5$ ([1]).

Our basic effective equation (8) for the averaged polymer chains vector position reads as

$$\frac{d}{dN} R_a(N) = -\beta \frac{A}{(R_1^2 + R_2^2)(N) + \delta^2} - \left(\frac{\gamma}{N}\right) R_a(N) \qquad (16.a)$$

$$\frac{d}{dN} R_3(N) = - \left(\frac{\gamma}{N}\right) R_3(N) \qquad (16.b)$$

where the subscript $a = 1, 2$ indexes the chain vector position components on the (x, y) plane.

In order to solve eq. (16a) at large N, we firstly consider the associated (ordinary) differential to the planar radius lenght $y(N) = (R_1^2 + R_2^2)(N)$ which is easily write down as follows

$$\frac{dy}{dN}(N) = -2\beta A \left(\frac{y}{y + \delta^2}\right)(N) = \left(\frac{\gamma}{N}\right) y(N) \tag{17}$$

Let us solve eq. (17) by means of a asymptotic series in the N-variable

$$y(N) = \frac{1}{N^{1+\omega}} \left[a(N) + \frac{b(N)}{N} + O\left(\frac{1}{N}\right)\right] \tag{18}$$

where the exponent $\omega > 0$ takes into account the approach to the equilibrium solution $g(N) \equiv 0$ of eq. (17) at $N \to \infty$. Let us note that one should only consider now the situation of zero "hard-core" monomer interaction $\delta^2 = 0$ and not before, since the differential equation makes sense only for $y(N) \neq 0$. Anyway, we always consider in the following discussion the case of a very small δ but non zero.

At large N, we can neglect the potential term in eq. (12) and obtain, thus, the behavior of the effective gaussian case ($A = 0$ in eq. (16a))

$$y(N) \sim N^{-\gamma} \tag{19}$$

After substituting eq. (19) into eq. (16a), we finally get the planar and z-axis large N behavior for the polymer chain averaged vector position components

$$R_a(N) \sim exp - \left(\frac{\beta A N}{\delta^2}\right) N^{-\gamma} \tag{20}$$

$$R_3(N) \sim N^{-\gamma} \tag{21}$$

From eq. (20), we can see a fastest exponential relaxation behavior to the "Effective" Gaussian case due to the presence of the experimental term $exp\left(-\dfrac{\beta A N}{\delta^2}\right)$.

The large N-behavior of the polymer chain giration radius is easily evaluated by means of eq. (14)

$$R^2(N) = N^{-\gamma} \left[\int^N (N')^{\gamma} \left(\sigma^2 - \frac{3\beta}{\delta} A(N')^{-2\gamma}\right)\right] \sim \frac{\sigma^2}{(\gamma + 1)} N + \left(-\frac{3AB}{\delta(1 - \gamma)}\right) N^{-2\gamma+1} \tag{22}$$

which by its turns shows that for large N the self-avoiding polymer chain with $\delta << \sigma^2$ reaches our further in the three-dimensional space than the usual Gaussian the relationship

effective chain, namely for large N, we have

$$R^2(N) - \left(\frac{\sigma^2}{\gamma+1}\right)N \geq N^{-2\gamma+1}\left(\frac{3A\beta}{\delta(\gamma-1)}\right) \tag{23}$$

an important qualitative result and strongly dependent of the self-ordinary interaction parameters (δ, γ) in a non-analytical way.

Acknowledgments

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