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RIGHTLY NORMALIZED END-TO-END DISTRIBUTION FUNCTION OF PARTIALLY FLEXIBLE POLYMERS

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A normalization problem is discussed, regarding the use of the Green function $G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0)$ in the statistical theory of configurations of a 'partially flexible polymer' of length L thermalized with its environment. The polymer is defined with a (constant) stiffness parameter $\eta > 0$. The Green function $G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0)$ is expressed as a path-integral with paths $\mathbf{r}(s), \mathbf{v}(s)$ in a 6-dimensional space $\{\mathbf{r},\mathbf{v}\}$, $\mathbf{v}(s) = \mathrm{d}\mathbf{r}(s)/\mathrm{d}s$. The basic question which the author analyzes in detail is the accommodation of the Green function $G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0)$ with the concept of the end-to-end probability density $P^{\mathrm{c}}(\mathbf{r},\vec{\Omega},L|\mathbf{r}_0,\vec{\Omega}_0)$ defined under the constraints $|\mathbf{v}| = |\mathbf{v}_0| = 1$. The vectors $\mathbf{r}$, $\mathbf{r}_0$ and the unit vectors $\mathbf{v} \equiv \vec{\Omega}$, $\mathbf{v}_0 \equiv \vec{\Omega}_0$ define, respectively, the positions and the tangential directions of the polymer ends. ($\mathbf{r}(0) = \mathbf{r}_0$, $\mathbf{r}(L) = \mathbf{r}$, $\mathbf{v}(0) = \vec{\Omega}_0$, $\mathbf{v}(L) = \vec{\Omega}$.) An explicit expression for $P^{\mathrm{c}}(\mathbf{r},\vec{\Omega},L|\mathbf{r}_0,\vec{\Omega}_0)$ is derived as a function of the stiffness parameter η and the temperature $T = 1/(k_{\mathrm{B}}\beta)$. An exact formula is derived for the mean-square end-to-end distance $\langle R^2\rangle_L$ as a function of η and β. A thorough description is presented concerning the statistics of the tangential direction $\vec{\Omega}$ of the polymer end with $s = L$ provided that the tangential direction $\vec{\Omega}_0$ is given. When elucidating this statistics, a special attention is devoted to very stiff polymers for which the author defines the 'paraxial approximation'.

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1 Introduction

The end-to-end distribution function of partially flexible polymers (or, tantamountly saying, of partially stiff polymers) can be expressed by means of a path integral in a 6-dimensional space [1, 2]. In the present paper, we will deal with partially flexible polymers defined with a given length $L > 0$ and a given stiffness parameter $\eta > 0$. If $\eta \to +0$, the polymers become entirely flexible, like threads. If $\eta \to \infty$, the polymers become entirely inflexible, like rigid rods.

In the limiting case when $\eta \to +0$, the end-to-end distribution function can be expressed by the path integral

$$P_{\mathrm{K}}(\mathbf{r},L|\mathbf{r}_0) = \mathcal{N}_{\mathrm{K}}(\lambda L) \int_{\mathbf{r}_0,0}^{\mathbf{r},L} \mathcal{D}\mathbf{r}(s)\, \exp\left[-\frac{3}{2\lambda}\int_0^L \mathrm{d}s \left(\frac{\mathrm{d}\mathbf{r}(s)}{\mathrm{d}s}\right)^2\right]. \tag{1}$$

The subscript K should suggest that integral (1) concerns the so-called Kuhn model. The parameter $\lambda > 0$ is the Kuhn effective length of monomers of which the polymer is composed. The prefactor $\mathcal{N}_{\mathrm{K}}(\lambda L) > 0$ is a normalization coefficient which may vary with the way of how the functional integration is carried out, but which, being dependent on the product λL, is independent of the position vectors $\mathbf{r}$ and $\mathbf{r}_0$ of the ends of the polymer. Formally, $P_{\mathrm{K}}(\mathbf{r}, L|\mathbf{r}_0)$ is the solution of the equation

$$\frac{\partial P_{\mathrm{K}}(\mathbf{r}, L|\mathbf{r}_0)}{\partial L} = \frac{\lambda}{6} \nabla^2 P_{\mathrm{K}}(\mathbf{r}, L|\mathbf{r}_0) \, , \tag{2}$$

respecting the 'initial' condition

$$P_{\mathrm{K}}(\mathbf{r}, +0|\mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0) \, . \tag{3}$$

The solution is a Gaussian:

$$P_{\mathrm{K}}(\mathbf{r}, L|\mathbf{r}_0) = \left(\frac{3}{2\pi\lambda L}\right)^{3/2} \exp\left[-\frac{3(\mathbf{r} - \mathbf{r}_0)^2}{2\lambda L}\right] . \tag{4}$$

This function expresses a probability density, since

$$\int \mathrm{d}^3 r \, P_{\mathrm{K}}(\mathbf{r}, L|\mathbf{r}_0) = 1 \, . \tag{5}$$

Let us now consider a statistical ensemble of polymers of the length L under the following three conditions:

(i) The polymers are only partially flexible, not interacting with each other, all characterized by the same stiffness parameter $\eta > 0$.

(ii) They are situated in a suspension held at a given temperature $T > 0$ in thermodynamic equilibrium.

(iii) They are extensible to a certain extent.

Then we can express the end-to-end distribution function of any polymer of this ensemble (taking this polymer as a probabilistic subject) as the path integral [1, 2]

$$G(\mathbf{r}, \mathbf{v}, L|\mathbf{r}_0, \mathbf{v}_0) = \mathcal{N}(\lambda L) \int_{\mathbf{r}_0, \mathbf{v}_0, 0}^{\mathbf{r}, \mathbf{v}, L} \mathcal{D}\mathbf{r}(s) \mathcal{D}\mathbf{v}(s) \, \delta\left(\mathbf{v}(s) - \frac{\mathrm{d}\mathbf{r}(s)}{\mathrm{d}s}\right)$$
$$\times \exp\left[-\frac{3}{2\lambda} \int_0^L \mathrm{d}s \left(\frac{\mathrm{d}\mathbf{r}(s)}{\mathrm{d}s}\right)^2\right] \exp\left[-\frac{\beta\eta}{2} \int_0^L \mathrm{d}s \left(\frac{\mathrm{d}\mathbf{v}(s)}{\mathrm{d}s}\right)^2\right] . \tag{6}$$

In the $\mathbf{v}$-integration, only those values of $\mathbf{v}(s)$ contribute to the value of integral (6) for which

$$\mathbf{v}(s) = \frac{\mathrm{d}\mathbf{r}(s)}{\mathrm{d}s} \, . \tag{7}$$

The expression $\frac{1}{2}\eta[\mathrm{d}\mathbf{v}/\mathrm{d}s]^2$ may be interpreted as the potential energy per unit length (in the Hookian approximation) if the polymer is taken as a bent elastic object. In general, the curvature of this object depends on the length parameter s and this dependence is given by the function $|\mathrm{d}\mathbf{v}(s)/\mathrm{d}s| = |\mathrm{d}^2\mathbf{r}(s)/\mathrm{d}s^2|$. The parameter $\beta > 0$ in expression (6) is the usual parameter of the statistical physics:

$$\beta = \frac{1}{k_{\mathrm{B}}T} \ . \tag{8}$$

The function $G(\mathbf{r}, \mathbf{v}, L|\mathbf{r}_0, \mathbf{v}_0)$ is expected to be proportional to a probability density defined in the sense of the Boltzmann statistics; hence the β-dependent exponential. The factor $\frac{1}{2}$ in the curvature-dependent exponent is a matter of the definition of the parameter η. In the spirit of the path-integral theory, we require that

$$G(\mathbf{r}, \mathbf{v}, +0|\mathbf{r}_0, \mathbf{v}_0) = \delta(\mathbf{r} - \mathbf{r}_0)\delta(\mathbf{v} - \mathbf{v}_0) \ . \tag{9}$$

The normalization coefficient $\mathcal{N}(\lambda L)$, which must be consistent with condition (9), is independent of the vectors

$$\mathbf{r}(0) = \mathbf{r}_0, \ \mathbf{v}(0) = \mathbf{v}_0, \ \mathbf{r}(L) = \mathbf{r}, \ \mathbf{v}(L) = \mathbf{v} \tag{10}$$

which are given in advance. If we want to transform expression (6) into a probability density, we must still multiply it with an additional normalizing factor. Namely, with the exception of the limiting case when $L \ \to \ +0$,

$$\int \mathrm{d}^3 r \ G(\mathbf{r}, \mathbf{v}, L|\mathbf{r}_0, \mathbf{v}_0) \ \neq \ 1 \ . \tag{11}$$

The symbols $\mathrm{d}\mathbf{r}(s)/\mathrm{d}s$ and $\mathrm{d}\mathbf{v}(s)/\mathrm{d}s$ occurring in the exponents of the Wiener (or Feynman) path integrals [3], do not signify the derivatives in the classical meaning of this notion. A typical path $\mathbf{r}(s), \mathbf{v}(s)$ involved in the path integration means actually a highly irregular continuos curve in the 6-dimensional phase space $\{\mathbf{r}, \mathbf{v}\}$. Mathematicians would say that the curve is ‘almost nowhere differentiable’. Even if we may consider a subset of paths $\mathbf{r}(s), \mathbf{v}(s)$ for which we may interpret $\dot{\mathbf{r}}(s), \dot{\mathbf{v}}(s)$ as derivatives (here the dot means the derivative with respect to the length parameter s), this subset is infinitely smaller than the set of the ‘almost nowhere differentiable’ paths.

This lesson used to make difficulties. Namely, the differential geometry tells us that if $\mathbf{r}(s)$ is any regular curve in the 3D space, then $\mathbf{v}(s) \ = \ \mathrm{d}\mathbf{r}(s)/\mathrm{d}s$ should be a unit vector tangential to the curve in the position s. From this reason, there were attempts (cf. e.g. [4]) to elaborate a theory of (partially) stiff polymers under the assumption of the validity of the equality $|\mathbf{v}(s)| = 1$ applied for all values $s \ \in \ (0, L)$. Obviously, this assumption would necessitate a revision of the path integral formalism even in the case of the Kuhn model (when $\eta \to +0$). Nevertheless, the end-to-end function $P_{\mathrm{K}}(\mathbf{r}, L|\mathbf{r}_0)$ did prove itself as a very successful approximation for some factual polymers. Therefore, the theoretical model with the equality $|\mathbf{v}(s)| \ = \ 1$, when required for *all* values of s, was not accepted by many (perhaps the majority of) theorists working in the polymer physics. Until now, polymer theorists seem to continue being on the horns of a dilemma, since to decide whether the formulation based on the path integral (6) is always better than the formulation according to which the polymers should rather be described as curves obeying precepts of the standard differential geometry is rather risky. (The author of the review paper [1] was evidently well conscious of this dilemma.) In this difficult situation, it is perhaps better to speak of models than to make universal and unequivocal conclusions.

In the present paper, we adopt the argument that actually s is a parameter *numbering* the monomers along the polymer and not primarily a length parameter. That is why $|\mathrm{d}\mathbf{r}(s)/\mathrm{d}s|$ need not be put equal to unity if $0 < s < L$. This argument was promoted by Harris and Hearst [5]. Agreeing with this argument, we require the fulfilment of the equality $|\mathbf{v}(s)| = 1$ only for the end points, i.e. for $s = 0$ and for $s = L$,

$$|\mathbf{v}(0)| = 1\ , \quad |\mathbf{v}(L)| = 1\ , \tag{12}$$

assuming that there is no necessity to pose any constraint on vectors $\mathbf{v}(s)$ if s a position in between. This viewpoint allows us duly to employ the path integration as is required by formula (6).

However, if $\mathbf{v}$, $\mathbf{v}_0$ are fixed unit vectors, we have to cogitate anew whether the function $G(\mathbf{r}, \mathbf{v}, L|\mathbf{r}_0, \mathbf{v}_0)$ itself, even if we multiply it by an adequate normalizing coefficient, can directly represent an end-to-end distribution function. There are two reasons for re-evaluation. First, if the values of $|\mathbf{v}|$ and $|\mathbf{v}_0|$ are put equal to unity in the function $G(\mathbf{r}, \mathbf{v}, L|\mathbf{r}_0, \mathbf{v}_0)$, the delta-function $\delta(\mathbf{v} - \mathbf{v}_0)$ defining the 'initial condition' (cf. equality (9)) loses its proper meaning. Second, the normalization of the end-to-end distribution function defined in the desired sense (namely, that it should mean a probability density) depends relevantly on the acceptance of the constraint $|\mathbf{v}| = 1$.

This is a problem that seems to have been neglected in the literature and we feel that its detailed clarification is fully justified.

2 End-to-end probability density in the 5D space $\{x, y, z, \vartheta, \varphi\}$

2.1 General definition of the probability density in the 5D space

In our calculation of the probability density as a function of the variables $\{x, y, z, \vartheta, \varphi\}$, we will proceed as follows.

The first step is to calculate the function $G(\mathbf{r}, \mathbf{v}, L|\mathbf{r}_0, \mathbf{v}_0)$ by calculating the path integral (6) and respecting condition (9). The calculation is to be done without any constraint on the variables v_x, v_y and v_z. (The vector $\mathbf{v}_0$ may always be arbitrary.)

The second step is to show which measures must be done if the path integral (6) is to be directly utilizable in the proper calculation of the end-to-end distribution function under the constraint defined by the equalities $|\mathbf{v}_0| = 1$, $|\mathbf{v}| = 1$. We will denote this end-to-end distribution function as $P^{\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$. The superscript 'c' in P^{c} should indicate the word constraint. (To avoid any misunderstanding, let us accentuate that we will not discuss any *topological* constraint, or any self-avoiding walks. These would deserve attention in their own right [2].) The vectors $\vec{\Omega}$ and $\vec{\Omega}_0$ symbolize the angular pairs (ϑ, φ) and (ϑ_0, φ_0) defining, respectively, the directions of the vectors $\mathbf{v}$ and $\mathbf{v}_0$.

When expressing $\mathbf{v}$ and $\mathbf{v}_0$ in spherical coordinates, $v_{0x} = v_0 \cos\varphi_0 \sin\vartheta_0$, $v_{0y} = v_0 \sin\varphi_0 \sin\vartheta_0$, $v_{0z} = v_0 \cos\vartheta_0$, $v_x = \cos\varphi \sin\vartheta$, $v_y = \sin\varphi \sin\vartheta$, $v_z = \cos\vartheta$, ($0 \le \varphi_0 < 2\pi$, $0 \le \varphi < 2\pi$, $0 \le \vartheta_0 < \pi$, $0 \le \vartheta < \pi$), we write G as $G(\mathbf{r}, v, \vec{\Omega}, L|\mathbf{r}_0, v_0, \vec{\Omega})$. (Let us repeat: the variables $v > 0$ and $v_0 > 0$ are not constrained if we have in mind the function G.)

Our *definition* of the function $P^{\mathrm{c}}(\mathbf{r},\vec{\Omega},L|\mathbf{r}_0,\vec{\Omega}_0)$ reads:

$$P^{\mathrm{c}}(\mathbf{r},\vec{\Omega},L|\mathbf{r}_0,\vec{\Omega}_0) = N\int_0^\infty \mathrm{d}v_0\, \Delta_\Gamma(v_0-1)\, G(\mathbf{r},v,\vec{\Omega},L|\mathbf{r}_0,v_0,\vec{\Omega}_0)\Big|_{v=1}. \tag{13}$$

In this integral, $\Delta_\Gamma(u)$ is a very narrow function centred in zero and equal to unity for $u = 0$. For instance, $\Delta_\Gamma(u) = \exp(-\,u^2/\Gamma^2)$ or $\Delta_\Gamma(u) = \Gamma^2/(u^2+\Gamma^2)$. The width of both these functions is equal (with a factor comparable to unity) to Γ. If $\Gamma \to +0$ and if these functions are multiplied with suitable prefactors (equal, respectively, to $1/\sqrt{\pi\Gamma^2}$ or to $1/(\pi\Gamma)$), we obtain two familiar representations of the delta-function $\delta(u)$. Nonetheless, if we had used a narrow Gaussian or Lorentzian in the role of $\Delta_\Gamma(v_0-1)$ in integral (13), their prefactors would be insignificant, as they could be absorbed in the normalizing constant $N > 0$. In any case, we assume that $0 < \Gamma \ll 1$. The choice of a *non-zero* (positive) value of Γ is explained by the existence of the uncertainty which one meets (as we have discussed in the Introduction) when one describes polymers in the framework of the path-integral formalism.

We require that

$$\int \mathrm{d}^3r \int \mathrm{d}^2\Omega\; P^{\mathrm{c}}(\mathbf{r},\vec{\Omega},L|\mathbf{r}_0,\vec{\Omega}_0) = 1\,, \tag{14}$$

where

$$\int \mathrm{d}^2\Omega = \int_0^{2\pi}\mathrm{d}\varphi \int_0^\pi \mathrm{d}\vartheta\, \sin\vartheta\,.$$

The normalizing coefficient $N > 0$ is then given by the expression

$$N = \left[\int_0^{2\pi}\mathrm{d}\varphi\int_0^\pi \mathrm{d}\vartheta\,\sin\vartheta\int \mathrm{d}^3r\int_0^\infty \mathrm{d}v_0\,\Delta_\Gamma(v_0-1)\; G(\mathbf{r},v,\vec{\Omega},L|\mathbf{r}_0,v_0,\vec{\Omega}_0)\Big|_{v=1}\right]^{-1}. \tag{15}$$

Setting the problem of the normalizing constant N aside for a while, let us now focus attention on the 'initial condition' which is prescribed for the function

$$G^{\mathrm{c}}(\mathbf{r},\vec{\Omega},L|\mathbf{r}_0,\vec{\Omega}_0) = \int_0^\infty \mathrm{d}v_0\,\Delta_\Gamma(v_0-1)\,G(\mathbf{r},v,\vec{\Omega},L|\mathbf{r}_0,v_0,\vec{\Omega}_0)\Big|_{v=1}. \tag{16}$$

Since the spherical coordinates are orthogonal, we may write down the identity

$$\delta(\mathbf{v}-\mathbf{v}_0) = \delta(v_x-v_{0x})\delta(v_y-v_{0y})\delta(v_z-v_{0z}) = \frac{1}{\sin\vartheta}\,\delta(v-v_0)\delta(\varphi-\varphi_0)\delta(\vartheta-\vartheta_0).$$

Thus, condition (9) implies that

$$G^{\mathrm{c}}(\mathbf{r},\vec{\Omega},+0|\mathbf{r}_0,\vec{\Omega}_0) = \frac{1}{\sin\vartheta}\,\delta(\mathbf{r}-\mathbf{r}_0)\delta(\varphi-\varphi_0)\delta(\vartheta-\vartheta_0) \;\equiv\; \delta(\mathbf{r}-\mathbf{r}_0)\delta(\vec{\Omega}-\vec{\Omega}_0). \tag{17}$$

2.2 The function $G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0)$

Owing to the symmetry of our problem, we may consider the factorization

$$G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0) = G^{1\mathrm{D}}(x,v,L|x_0,v_{0x})G^{1\mathrm{D}}(y,v,L|y_0,v_{0y})G^{1\mathrm{D}}(z,v,L|z_0,v_{0z}) \ . \quad (18)$$

The Lagrangian of the path integral

$$G^{1\mathrm{D}}(x,v_x,L|x_0,v_{0x}) = [\mathcal{N}(\lambda L)]^{1/3} \int_{x_0,v_{0x},0}^{x,v_x,L} \mathcal{D}x(s)\mathcal{D}v_x(s)\,\delta\left(v_x(s) - \frac{\mathrm{d}x(s)}{\mathrm{d}s}\right)$$
$$\times\ \exp\left[-\ \frac{3}{2\lambda}\int_0^L \mathrm{d}s\left(\frac{\mathrm{d}x(s)}{\mathrm{d}s}\right)^2 -\ \frac{\beta\eta}{2}\int_0^L \mathrm{d}s\left(\frac{\mathrm{d}v_x(s)}{\mathrm{d}s}\right)^2\right] , \quad (19)$$

is quadratic, so its calculation can be carried out completely in an analytical manner. The path integral (19) can be expressed (cf. Kleinert's paper [6]) as the Fourier transform

$$G^{1\mathrm{D}}(x,v_x,L|x_0,v_{0x}) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}p\ \exp[-\,\mathrm{i}p\,(x-x_0)]\ R_p(v_x,L|v_{0x}) \ , \quad (20)$$

where $R_p(v_x,L|v_{0x})$ is the 'propagator' of a 'shifted oscillator':

$$R_p(v_x,L|v_{0x}) = \mathcal{N}_{\mathrm{osc}} \int_{v_{0x},0}^{v_x,L}\mathcal{D}v_x(s)$$
$$\times\ \exp\left\{-\ \frac{\beta\eta}{2}\int_0^L \mathrm{d}s\left[\left(\frac{\mathrm{d}v_x(s)}{\mathrm{d}s}\right)^2 + K^2[v_x(s)]^2\right] -\ \mathrm{i}p\int_0^L \mathrm{d}s\ v_x(s)\right\} . \quad (21)$$

The 'mass' of this oscillator problem is equal to $\beta\eta$. The oscillator is defined with the 'frequency parameter'

$$K = \sqrt{\frac{3}{\lambda\beta\eta}} \ . \quad (22)$$

(We use intentionally different symbols from Kleinert's [6]. Both the 'mass' $\beta\eta$ and the 'time variable' s is measured in meters whilst the 'frequency parameter' K and the variable p are measured in m^{-1}. The variable $v_x(s)$ is dimensionless.) We require the 'initial condition'

$$R_p(v_x,+0|v_{0x}) = \delta(v_x - v_{0x}) \quad (23)$$

and this is consistent with the condition

$$G^{1\mathrm{D}}(x,v_x,+0|x_0,v_{0x}) = \delta(x-x_0)\delta(v_x-v_{0x}) \ . \quad (24)$$

In particular, if $p=0$, we write

$$R_0(v_x,L|v_{0x}) = G^{1\mathrm{D}}_{\mathrm{osc}}(v_x,L|v_{0x}) \ . \quad (25)$$

The analytical form of the oscillator propagator is well known [3]. With our symbols, we write it as the function

$$G^{1\mathrm{D}}_{\mathrm{osc}}(v_x,L|v_{0x}) =$$

$$\sqrt{\frac{\beta\eta K}{2\pi \sinh(KL)}}\ \exp\left[-\ \frac{\beta\eta K}{2\sinh(KL)}\left[\cosh(KL)(v_x^2+v_{0x}^2)-2v_{0x}v_x\right]\right]. \tag{26}$$

With a general (real) value of p, we write

$$R_p(v_x,L|v_{0x})=\exp\left(-\ \frac{Lp^2}{2\beta\eta K^2}\right)G^{1\mathrm{D}}_{\mathrm{osc}}\left(v_x\ +\ \frac{\mathrm{i}p}{\beta\eta K^2}\,,L\,\middle|\,v_{0x}\ +\ \frac{\mathrm{i}p}{\beta\eta K^2}\right). \tag{27}$$

(This corresponds to oscillations realized along a straight line parallel to the real axis on the complex v_x-plane.) Thereupon

$$R_p(v_x,L|v_{0x})=G^{1\mathrm{D}}_{\mathrm{osc}}(v_x,L|v_{0x})\times$$

$$\exp\left[-\ \frac{L}{2\beta\eta K^2}\left[1\ -\ \mu(KL)\right]p^2\right]\ \exp\left[-\ \mathrm{i}\,\frac{L\,\mu(KL)}{2}\,(v_x+v_{0x})\,p\right], \tag{28}$$

where

$$\mu(KL)=\frac{\tanh(KL/2)}{KL/2}\ . \tag{29}$$

Expression (28) is a Gaussian in the variable p and so, when we insert it in integral (20), we can easily cope with the integration. The result of this integration reads:

$$G^{1\mathrm{D}}(x,v_x,L|x_0,v_{0x})=\sqrt{\frac{\beta\eta K}{2\pi\sinh(KL)}}\sqrt{\frac{\beta\eta K^2}{2\pi L\left[1-\mu(KL)\right]}}\times$$

$$\exp\left\{-\ \frac{\beta\eta K}{2\sinh(KL)}\left[\cosh(KL)\,(v_x^2+v_{0x}^2)-2v_xv_{0x}\right]\right.$$

$$\left.-\ \frac{\beta\eta K^2}{2L\left[1-\mu(KL)\right]}\left[x-x_0\ +\ \frac{L\,\mu(KL)}{2}\,(v_x+v_{0x})\right]^2\right\}. \tag{30}$$

This function represents the fundamental solution (i.e. Green's function) of the equation

$$\frac{\partial G^{1\mathrm{D}}(x,v_x,L|x_0,v_{0x})}{\partial L}=\frac{1}{2\beta\eta}\,\frac{\partial^2G^{1\mathrm{D}}(x,v_x,L|x_0,v_{0x})}{\partial v_x^2}$$

$$-\ \frac{\beta\eta K^2}{2}\,v_x^2\,G^{1\mathrm{D}}(x,v_x,L|x_0,v_{0x})\ -\ v_x\,\frac{\partial G^{1\mathrm{D}}(x,v_x,L|x_0,v_{0x})}{\partial x}\ . \tag{31}$$

Obviously, the functions $G^{1\mathrm{D}}(y,v_y,L|y_0,v_{0y})$ and $G^{1\mathrm{D}}(z,v_z,L|z_0,v_{0z})$ are given by the same formula (30), only each x has to be replaced by y and z, respectively. Then we may state that the end-to-end distribution function $G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0)$ is the fundamental solution of the equation

$$\frac{\partial G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0)}{\partial L}=\frac{1}{2\beta\eta}\,\nabla^2_{\mathbf{v}}G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0)$$

$$- \frac{\beta\eta K^2}{2}\, v^2\, G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0) \;-\; \mathbf{v}.\nabla_{\mathbf{r}} G_0(\mathbf{r},\mathbf{v}_x,L|\mathbf{r}_0,\mathbf{v}_0)\;, \tag{32}$$

($v^2 = |\mathbf{v}|^2$) satisfying condition (9). Thus, in the 3D case, we have got the function

$$G(\mathbf{r},\mathbf{v},L|\mathbf{r}_0,\mathbf{v}_0) = \left[\frac{\beta\eta K}{2\pi \sinh(KL)}\right]^{3/2} \left[\frac{\beta\eta K^2}{2\pi L\,[1-\mu(KL)]}\right]^{3/2} \times$$

$$\exp\left\{ -\; \frac{\beta\eta K}{2\sinh(KL)}\left[\cosh(KL)\,(v^2+v_0^2) - 2\mathbf{v}.\mathbf{v}_0\right]\right.$$

$$\left. - \frac{\beta\eta K^2}{2L\,[1-\mu(KL)]}\left[\mathbf{r}-\mathbf{r}_0 \;+\; \frac{L\,\mu(KL)}{2}\,(\mathbf{v}+\mathbf{v}_0)\right]^2\right\}. \tag{33}$$

This function is translationally and rotationally invariant. Therefore, we do not lose generality if we employ new variables so that the vector $\mathbf{r}-\mathbf{r}_0$ may lie in the positive direction of the z-axis and the vector $\mathbf{v}_0$ may lie in the plane (x,z). The new variables will be distinguished from the old ones by the tilde:

$$\tilde{x} = \tilde{y} = \tilde{x}_0 = \tilde{y}_0 = 0\;, \quad \tilde{z} = |\mathbf{r}-\mathbf{r}_0|\;, \quad \tilde{\varphi}_0 = 0\;. \tag{34}$$

Obviously,

$$\tilde{v}_0 = v_0, \quad \tilde{v} = v\;. \tag{35}$$

After defining the directional angles of the vector $\mathbf{r}-\mathbf{r}_0$ in the old coordinate system,

$$x - x_0 = |\mathbf{r}-\mathbf{r}_0|\; \sin\Theta\; \cos\Phi,$$

$$y - y_0 = |\mathbf{r}-\mathbf{r}_0|\; \sin\Theta\; \sin\Phi,$$

$$z - z_0 = |\mathbf{r}-\mathbf{r}_0|\; \cos\Theta,$$

$$v_{0x} = v_0\; \sin\vartheta_0\; \cos\varphi_0, \quad v_{0y} = v_0\; \sin\vartheta_0\; \sin\varphi_0, \quad v_{0z} = v_0\; \cos\vartheta_0\;, \tag{36}$$

we define the components $\tilde{v}_x$, $\tilde{v}_y$ and $\tilde{v}_z$ of the vector $\mathbf{v}$ in the new coordinate system by the equations

$$\begin{aligned} v_x &= \cos\Theta\cos(\varphi_0-\Phi)\,\tilde{v}_x - \sin(\varphi_0-\Phi)\,\tilde{v}_y + \sin\Theta\cos\varphi_0\,\tilde{v}_z\;,\\ v_y &= \cos\Theta\sin(\varphi_0-\Phi)\,\tilde{v}_x + \cos(\varphi_0-\Phi)\,\tilde{v}_y + \sin\Theta\sin(\varphi_0-\Phi)\,\tilde{v}_z\;,\\ v_z &= -\sin\Theta\,\tilde{v}_x + \cos\Theta\,\tilde{v}_z\;. \end{aligned} \tag{37}$$

Using the new spherical angles, we write

$$\tilde{v}_{0x} = v_0 \sin\tilde{\vartheta}_0\;, \quad \tilde{v}_{0y} = 0\;, \quad \tilde{v}_{0z} = v_0\cos\tilde{\vartheta}_0\;, \tag{38}$$

$$\tilde{v}_x = v\;\sin\tilde{\vartheta}\cos\tilde{\varphi}, \quad \tilde{v}_y = v\;\sin\tilde{\vartheta}\sin\tilde{\varphi}, \quad \tilde{v}_z = v\;\cos\tilde{\vartheta}\;. \tag{39}$$

Then

$$(\mathbf{v}+\mathbf{v}_0)^2 = (\tilde{\mathbf{v}}+\tilde{\mathbf{v}}_0)^2 = v^2 + v_0^2 + 2\tilde{\mathbf{v}}.\tilde{\mathbf{v}}_0 \ , \tag{40}$$

where

$$\tilde{\mathbf{v}}.\tilde{\mathbf{v}}_0 = \mathbf{v}.\mathbf{v}_0 = v v_0 \left(\sin\tilde{\vartheta}_0 \sin\tilde{\vartheta}\cos\tilde{\varphi} + \cos\tilde{\vartheta}_0\cos\tilde{\vartheta}\right) \ , \tag{41}$$

and

$$(\mathbf{r}-\mathbf{r}_0).(\mathbf{v}+\mathbf{v}_0) = (\tilde{\mathbf{r}}-\tilde{\mathbf{r}}_0).(\tilde{\mathbf{v}}+\tilde{\mathbf{v}}_0) = |\mathbf{r}-\mathbf{r}_0|(\tilde{v}_z+\tilde{v}_{0z}) = |\mathbf{r}-\mathbf{r}_0|(v\cos\tilde{\vartheta}+v_0\cos\tilde{\vartheta}_0) . \tag{42}$$

Employing these results, we can rewrite formula (33) in the form

$$\begin{aligned}
&\tilde{G}(\mathbf{r}, v, \tilde{\vartheta}, \tilde{\varphi}, L|\mathbf{r}_0, v_0, \tilde{\vartheta}_0, 0) = \\
&\left[\frac{\beta\eta K}{2\pi \sinh(KL)}\right]^{3/2} \left[\frac{\beta\eta K^2}{2\pi L\,[1-\mu(KL)]}\right]^{3/2} \exp\left[-\ \frac{\beta\eta K^2}{2L\,[1-\mu(KL)]}\,(\mathbf{r}-\mathbf{r}_0)^2\right] \\
&\times\ \exp\left[-\ \frac{\beta\eta K}{2}\left(\mathrm{cotanh}(KL)\ +\ \frac{KL\,[\mu(KL)]^2}{4\,[1-\mu(KL)]}\right)(v^2+v_0^2)\right] \times \\
&\exp\left[-\beta\eta K\left(\frac{KL\,[\mu(KL)]^2}{4\,[1-\mu(KL)]}\ -\ \frac{1}{\sinh(KL)}\right)\right] v v_0 \left(\sin\tilde{\vartheta}_0\sin\tilde{\vartheta}\cos\tilde{\varphi} + \cos\tilde{\vartheta}_0\cos\tilde{\vartheta}\right)\Big] \\
&\times\ \exp\left[-\ \frac{\beta\eta K^2 \mu(KL)\,|\mathbf{r}-\mathbf{r}_0|}{2\,[1-\mu(KL)]}\ (v\cos\tilde{\vartheta}+v_0\cos\tilde{\vartheta}_0)\right] .
\end{aligned} \tag{43}$$

(If $\tilde{\varphi}_0 \neq 0$, then $\tilde{\varphi}$ in formula (43) has to be replaced by $\tilde{\varphi}-\tilde{\varphi}_0$.)
This seemingly formidable function is actually a Gaussian in the variables v, v_0 and $|\mathbf{r}-\mathbf{r}_0|$.

2.3 The function $G^{\,\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$

The width of the Gaussian in the variable v_0 in expression (43) increases if the length L increases. In any case, with the exception of the limiting case when L is infinitesimally small, the width of this Gaussian is much greater than the parameter Γ corrresponding to the width of the function $\Delta(u)$. That is why we may replace the variable v_0 by unity. As we have discussed above, if Γ is sufficiently small, we may consider $\alpha\Delta(u)/\Gamma$ as a function approximating very well the Dirac delta-function. ($\alpha > 0$ is a numerical factor of the order of magnitude of unity.) Thus, when using expression (43), we arrive, according to formula (16), at the function

$$\begin{aligned}
&G^{\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0) = \frac{\Gamma}{\alpha}\left[\frac{\beta\eta K}{2\pi\sinh(KL)}\right]^{3/2}\left[\frac{\beta\eta K^2}{2\pi L\,[1-\mu(KL)]}\right]^{3/2} \times \\
&\exp\left[-\beta\eta K\left(\mathrm{cotanh}(KL) + \frac{KL\,[\mu(KL)]^2}{4\,[1-\mu(KL)]}\right)\right] \exp\left[-\ \frac{\beta\eta K^2}{2L\,[1-\mu(KL)]}(\mathbf{r}-\mathbf{r}_0)^2\right] \\
&\times\ \exp\left[-\ \beta\eta K\left(\frac{KL\,[\mu(KL)]^2}{4\,[1-\mu(KL)]}\ -\ \frac{1}{\sinh(KL)}\right)\right]\left(\sin\tilde{\vartheta}_0\sin\tilde{\vartheta}\cos\tilde{\varphi} + \cos\tilde{\vartheta}_0\cos\tilde{\vartheta}\right)\Big]
\end{aligned}$$

$$\times\ \exp\left[-\ \frac{\beta\eta K^2\mu(KL)\,|\mathbf{r}-\mathbf{r}_0|}{2\,[1-\mu(KL)]}\ (\cos\tilde{\vartheta}+\cos\tilde{\vartheta}_0)\right] \tag{44}$$

which can also be written as

$$G^{\rm c}(\mathbf{r},\vec{\Omega},L|\mathbf{r}_0,\vec{\Omega}_0) = \frac{\Gamma}{\alpha}\ \exp\left[-\ \beta\eta K\ {\rm cotanh}(KL)\right]$$
$$\times\left[\frac{\beta\eta K}{2\pi{\rm sinh}(KL)}\right]^{3/2}\left[\frac{\beta\eta K^2}{2\pi L\,[1-\mu(KL)]}\right]^{3/2}\ \exp\left[\frac{\beta\eta K}{{\rm sinh}(KL)}\ \vec{\Omega}.\vec{\Omega}_0\right]$$
$$\times\ \exp\left\{-\ \frac{\beta\eta K^2}{2L\,[1-\mu(KL)]}\left[\mathbf{r}-\mathbf{r}_0\ +\ \frac{L\mu(KL)}{2}\,(\vec{\Omega}+\vec{\Omega}_0)\right]^2\right\}. \tag{45}$$

2.4 The normalization coefficient N

It is easy to integrate the function $G^{\rm c}(\mathbf{r},\vec{\Omega},L|\mathbf{r}_0,\vec{\Omega}_0)$ with respect to the radiusvector $\mathbf{r}$:

$$\int {\rm d}^3r\ G^{\rm c}(\mathbf{r},\vec{\Omega},L|\mathbf{r}_0,\vec{\Omega}_0) = \frac{\Gamma}{\alpha}\ \exp\left[-\ \beta\eta K{\rm cotanh}(KL)\right]\left[\frac{\beta\eta K}{2\pi{\rm sinh}(KL)}\right]^{3/2}$$
$$\times\ \exp\left[\frac{\beta\eta K}{{\rm sinh}(KL)}\,[\sin\tilde{\vartheta}_0\sin\tilde{\vartheta}\cos(\tilde{\varphi}-\tilde{\varphi}_0)+\cos\tilde{\vartheta}_0\cos\tilde{\vartheta}]\right]. \tag{46}$$

According to formula (41), $\vec{\Omega}.\vec{\Omega}_0 = \sin\tilde{\vartheta}_0\sin\tilde{\vartheta}\cos(\tilde{\varphi}-\tilde{\varphi}_0)+\cos\tilde{\vartheta}_0\cos\tilde{\vartheta}$. The scalar product of two vectors is invariant with respect to rotations. So, we may make the z-axis parallel with the unit vector $\vec{\Omega}_0$. In this way, we obtain a new coordinate system. When introducing the spherical angles ϑ' and φ' of the vector $\vec{\Omega}$ in this new coordinate system, we state that $\vec{\Omega}.\vec{\Omega}_0 = \cos\vartheta'$ and since ${\rm d}^2\Omega = {\rm d}^2\Omega\,'$, we find that, when calculating the normalization coefficient N according to formula (15), the angular integration is reduced to the calculation of the integral

$$F(C) = \int {\rm d}^2\Omega\ \exp(C\ \vec{\Omega}.\vec{\Omega}_0) = \int_0^{2\pi}{\rm d}\varphi'\int_0^{\pi}{\rm d}\vartheta'\sin\vartheta'\ \exp(C\ \cos\vartheta')$$

with

$$C = \frac{\beta\eta K}{{\rm sinh}(KL)}\ .$$

Thereafter,

$$\int_0^{2\pi}{\rm d}\tilde{\varphi}\int_0^{\pi}{\rm d}\tilde{\vartheta}\ \sin\tilde{\vartheta}\ \exp\left[\frac{\beta\eta K}{{\rm sinh}(KL)}\,[\sin\tilde{\vartheta}_0\sin\tilde{\vartheta}\cos(\tilde{\varphi}-\tilde{\varphi}_0)+\cos\tilde{\vartheta}_0\cos\tilde{\vartheta}]\right]$$
$$=\ 4\pi\ \frac{{\rm sinh}(KL)}{\beta\eta K}\ {\rm sinh}\left(\frac{\beta\eta K}{{\rm sinh}(KL)}\right)\ . \tag{47}$$

Thus, finally we obtain the normalization coefficient

$$N =$$
$$\frac{1}{4\pi}\ \frac{\alpha}{\Gamma}\ \frac{\beta\eta K\exp\left[\beta\eta K{\rm cotanh}(KL)\right]}{{\rm sinh}(KL)}\left[{\rm sinh}\left(\frac{\beta\eta K}{{\rm sinh}(KL)}\right)\right]^{-1}\left[\frac{\beta\eta K}{2\pi{\rm sinh}(KL)}\right]^{-3/2}. \tag{48}$$

2.5 2.5. The function $P^{\,c}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$

Let us now summarize our results. For the probability density

$$P^{c}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0) = N\, G^{c}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)\ , \tag{49}$$

we have obtained the expression

$$P^{c}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0) =$$

$$\frac{1}{4\pi}\, \frac{\beta\eta K}{\sinh(KL)} \left[\sinh\left(\frac{\beta\eta K}{\sinh(KL)}\right)\right]^{-1} \exp\left(\frac{\beta\eta K}{\sinh(KL)}\, \vec{\Omega}.\vec{\Omega}_0\right)$$

$$\left[\frac{\beta\eta K^2}{2\pi L\,[1-\mu(KL)]}\right]^{3/2} \exp\left\{-\,\frac{\beta\eta K^2}{2L\,[1-\mu(KL)]}\left[\mathbf{r}-\mathbf{r}_0+\frac{L\mu(KL)}{2}(\vec{\Omega}+\vec{\Omega}_0)\right]^2\right\} , \tag{50}$$

$\vec{\Omega} = (\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta)$ and $\vec{\Omega}_0 = (\sin\vartheta_0\cos\varphi_0, \sin\vartheta_0\sin\varphi_0, \cos\vartheta_0)$. (Now we assume that the spherical angles are defined in an arbitrary coordinate system. We have not labelled these angles with the tilde since generally the direction of the z-axis need not be identical with the direction of the vector $\mathbf{r} - \mathbf{r}_0$.) Explicitly,

$$\vec{\Omega}.\vec{\Omega}_0 = \sin\vartheta_0 \sin\vartheta \cos(\varphi - \varphi_0) + \cos\vartheta_0 \cos\vartheta\ . \tag{51}$$

In the Kuhn limit, when $\eta \to +0$,

$$P^{c}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0) = \frac{1}{4\pi}\, P_{\mathrm{K}}(\mathbf{r}, L|\mathbf{r}_0)\ . \tag{52}$$

In this limit, the probability density $P^{c}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$ becomes isotropic. The denominator 4π means that the tangential directions of the polymer end with $s = L$ can fall with the same probability, equal to $\mathrm{d}^2\Omega/(4\pi)$, into each elementary space angle $\mathrm{d}^2\Omega$. To verify that formula (52) is correct, let us recall formula (22) defining the 'frequency' K. Then,

$$\beta\eta K^2 = \frac{3}{\lambda} \tag{53}$$

($\eta > 0, \beta > 0$. If $\eta \to +0$, we observe that

$$\mu(KL)\ \sim\ \sqrt{\eta}\ \to\ 0\ ,\quad \frac{\beta\eta K}{\sinh(KL)}\ \to\ 0\ ,\quad \frac{\beta\eta K}{\sinh(KL)}\left[\sinh\left(\frac{\beta\eta K}{\sinh(KL)}\right)\right]^{-1}\ \to\ 1\ .$$

3 Two examples of the use of the function $P^{\,c}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$

3.1 The mean-square end-to-end distance

We will now apply the end-to-end probability density (50) in the calculation of the mean-square end-to-end distance

$$\langle R^2\rangle_L = \int \mathrm{d}^2\Omega \int \mathrm{d}^3 r\ (\mathbf{r}-\mathbf{r}_0)^2\ P^{c}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)\ . \tag{54}$$

Obviously, the quantity $\langle R^2\rangle_L$ depends, for a given length L, on the stiffness parameter η of the polymer under consideration and on the temperature.

We can easily manage the $\mathbf{r}$-integration:

$$\left(\frac{A}{\pi}\right)^{3/2} \int \mathrm{d}^3 r\ (\mathbf{r}-\mathbf{r}_0)^2\ \exp[-\,A\,(\mathbf{r}-\mathbf{r}_0+\mathbf{B})^2] = \frac{3}{2A}\ +\ B^2\ . \tag{55}$$

(Here $A > 0$ and $B = |\mathbf{B}|$.) In our case, $\mathbf{B} = \frac{1}{2}L\mu(KL)(\vec{\Omega}+\vec{\Omega}_0)$, so that $B^2 = \frac{1}{2}L^2[\mu(KL)]^2\times(1+\vec{\Omega}.\vec{\Omega}_0)$. Therefore,

$$\begin{aligned}
&\left[\frac{\beta\eta K^2}{2\pi L\,[1-\mu(KL)]}\right]^{3/2} \int \mathrm{d}^3 r\ (\mathbf{r}-\mathbf{r}_0)^2 \\
&\times\ \exp\left\{-\ \frac{\beta\eta K^2}{2L\,[1-\mu(KL)]}\left[\mathbf{r}-\mathbf{r}_0\ +\ \frac{L\mu(KL)}{2}\,(\vec{\Omega}+\vec{\Omega}_0)\right]^2\right\} \\
&= \frac{3L\,[1-\mu(KL)]}{\beta\eta K^2}\ +\ \frac{L^2[\mu(KL)]^2}{2}\,(1+\vec{\Omega}.\vec{\Omega}_0)\ .
\end{aligned} \tag{56}$$

Hence,

$$\begin{aligned}
\langle R^2\rangle_L &= \frac{1}{4\pi}\,\frac{\beta\eta K}{\sinh(KL)}\left[\sinh\!\left(\frac{\beta\eta K}{\sinh(KL)}\right)\right]^{-1}\times \\
&\int \mathrm{d}^2\Omega\ \exp\left(\frac{\beta\eta K}{\sinh(KL)}\,\vec{\Omega}.\vec{\Omega}_0\right)\left[\frac{3L\,[1-\mu(KL)]}{\beta\eta K^2}\ +\ \frac{L^2[\mu(KL)]^2}{2}\,(1+\vec{\Omega}.\vec{\Omega}_0)\right].
\end{aligned} \tag{57}$$

This formula involves the following integrals:

$$\int \mathrm{d}^2\Omega\ \exp(C\,\vec{\Omega}.\vec{\Omega}_0) = 2\pi\int_0^\pi \mathrm{d}\vartheta\ \sin\vartheta\ \exp(C\cos\vartheta) = 4\pi\,\frac{\sinh C}{C} \tag{58}$$

(cf. formula (47)) and

$$\begin{aligned}
&\int \mathrm{d}^2\Omega\ \vec{\Omega}.\vec{\Omega}_0\ \exp(C\,\vec{\Omega}.\vec{\Omega}_0) = 2\pi\int_0^\pi \mathrm{d}\vartheta\ \sin\vartheta\cos\vartheta\ \exp(C\ \cos\vartheta) \\
&= 4\pi\,\frac{\mathrm{d}}{\mathrm{d}C}\,\frac{\sinh C}{C} = \frac{4\pi}{\mathrm{C}}\left(\cosh C\ -\ \frac{\sinh C}{C}\right)\ .
\end{aligned} \tag{59}$$

When all these relations are put together, we obtain the expression

$$\begin{aligned}
\langle R^2\rangle_L &= \frac{3L\,[1-\mu(KL)]}{\beta\eta K^2} + \frac{L^2[\mu(KL)]^2}{2} \\
&+ \frac{L^2[\mu(KL)]^2}{2}\left[\mathrm{cotanh}\!\left(\frac{\beta\eta K}{\sinh(KL)}\right)\ -\ \frac{\sinh(KL)}{\beta\eta K}\right]\ .
\end{aligned} \tag{60}$$

(Recall that $\mu(KL)$ was defined by expression (29).)

Let us now discuss the limiting case of very small values of the stiffness parameter η. If $\eta \to +0$, then $K \sim 1/\sqrt{\eta} \to \infty$ and $\mu(KL) \sim \sqrt{\eta} \to$ +0. (Do not forget the definition of K by expression (22).) Therefore, the expression inside the large brackets [ ] of the second term of expression (60) vanishes. Moreover, according to equation (29), $[\mu(KL)]^\alpha \to +0$ for $\eta \to +0$ if $\alpha > 0$ and so we conclude that also all the terms involving $\mu(KL)$ vanish. In this way, we have shown that

$$\frac{1}{L} \lim_{\eta \to +0} \langle R^2 \rangle_L = \lambda \ . \tag{61}$$

Of course, this result could be obtained directly by employing the probability density $P_\mathrm{K}(\mathbf{r}, L|\mathbf{r}_0)$ in the Kuhn theory. (Equality (61) justifies why λ has been called the *effective* Kuhn length.)

By the same token,

$$\frac{1}{L} \lim_{\beta \to +0} \langle R^2 \rangle_L = \lambda \ . \tag{62}$$

This means that if the temperature T is extremely high, the (partially) stiff polymers, with any value of η, should behave as ideally flexible polymers. (The temperature will overcome their stiffness.)

3.2 Statistics of the tangential directions of the polymer end with $s = L$

We define the reduced probability density

$$P^\mathrm{c}_\mathrm{ang}(\vec{\Omega}, L|\vec{\Omega}_0) = \int \mathrm{d}^3 r \; P^\mathrm{c}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0) \ . \tag{63}$$

After inserting expression (50) here, we find that

$$P^\mathrm{c}_\mathrm{ang}(\vec{\Omega}, L|\vec{\Omega}_0) = \frac{1}{4\pi} \frac{\beta\eta K}{\sinh(KL)} \left[\sinh\left(\frac{\beta\eta K}{\sinh(KL)} \right) \right]^{-1} \exp\left(\frac{\beta\eta K}{\sinh(KL)} \; \vec{\Omega}.\vec{\Omega}_0 \right) . \tag{64}$$

Without loss of generality, we may orient the unit vector $\vec{\Omega}_0$ in the positive direction of the z-axis. Then the spherical angle ϑ defining the direction of the vector $\vec{\Omega}$ is identical with the angle between the vectors $\vec{\Omega}$ and $\vec{\Omega}_0$. Thus, we may write

$$\begin{aligned} P^\mathrm{c}_\mathrm{ang}(\vec{\Omega}, L|\vec{\Omega}_0) &= \tilde{P}^\mathrm{c}_\mathrm{ang}(\vartheta, L) \\ &= \frac{1}{4\pi} \frac{\beta\eta K}{\sinh(KL)} \left[\sinh\left(\frac{\beta\eta K}{\sinh(KL)} \right) \right]^{-1} \exp\left(\frac{\beta\eta K}{\sinh(KL)} \; \cos\vartheta \right) , \end{aligned} \tag{65}$$

$0 \le \vartheta \le \pi$.

The first natural question that we pose concerns the mean value of the vector

$$\vec{\Omega}_\perp = (\sin\vartheta \cos\varphi, \sin\vartheta \sin\varphi, 0) \ . \tag{66}$$

This vector equals the projection of the vector $\vec{\Omega}$ onto the plane perpendicular to the vector $\vec{\Omega}_0$. Clearly,

$$\langle \vec{\Omega}_\perp \rangle = \int \mathrm{d}^2 \Omega \; \vec{\Omega}_\perp \; \tilde{P}^\mathrm{c}_\mathrm{ang}(\vartheta, L) = 0 \ , \tag{67}$$

since the integration with respect to φ gives zero:

$$\int_0^{2\pi} \mathrm{d}\varphi \, \cos\varphi = \int_0^{2\pi} \mathrm{d}\varphi \, \sin\varphi = 0 \, .$$

However, the mean value $\cos\vartheta$ is not equal to zero since the initial end (with $s = 0$) of the polymer dictates somewhat (owing to the stiffness of the polymer) its direction to the distant end (with $s = L$). If we consider $\vec{\Omega}$ and $\vec{\Omega}_0$ as unit vectors corresponding to two random directions, then, in fact, the integral

$$W(L) = \int \mathrm{d}^2\Omega \; \vec{\Omega}.\vec{\Omega}_0 \; P^{\mathrm{c}}_{\mathrm{ang}}(\vec{\Omega}, L|\vec{\Omega}_0) = 2\pi \int_0^{\pi} \mathrm{d}\vartheta \; \sin\vartheta \; \cos\vartheta \; \tilde{P}^{\mathrm{c}}_{\mathrm{ang}}(\vartheta, L|\vartheta_0) \qquad (68)$$

may be interpreted as their correlation function. We have already calculated this integral above (cf. formula (59)). We can readily write down the result:

$$W(L) = \mathrm{cotanh}\left(\frac{\beta\eta K}{\sinh(KL)}\right) - \frac{\sinh(KL)}{\beta\eta K} \, , \qquad (69)$$

or (after substituting expression (22) for K)

$$W(L) = \mathrm{cotanh}\left[\sqrt{\frac{3\beta\eta}{\lambda}}\Big/\sinh\left(\sqrt{\frac{3}{\lambda\beta\eta}}\, L\right)\right] - \sqrt{\frac{\lambda}{3\beta\eta}}\,\sinh\left(\sqrt{\frac{3}{\lambda\beta\eta}}\, L\right) . \qquad (70)$$

[Let us point out that the function $\mathcal{L}(u) = \mathrm{cotanh}\, u - 1/u$ occurs in the theory of electric (magnetic) dipoles in an electric (magnetic) field in thermodynamic equilibrium. If this field is oriented in the direction of the z-axis, the averaged value of the z-component of the polarization (magnetization) vector is proportional (as was shown first by Langevin) to the function $\mathcal{L}(u)$ with $u = \beta pE$ ($u = \beta pB$) where p is the electric (magnetic) dipole moment.]

The function $W(L)$ behaves normally as a legitimate (auto)correlation function, since, as one can show at once,

$$\lim_{L \to +0} W(L) = 1 \qquad (71)$$

and

$$\lim_{L \to \infty} W(L) = 0 \, . \qquad (72)$$

Equations (72) and (73) mean that the end-point tangential directions of the polymer are most correlated if $L \to +0$ (namely, then both the directions are identical, provided that $\eta > 0$), and that there is no correlation between them if $L \to \infty$.

From formula (71), we deduce also that

$$\lim_{\eta \to +0} W(L) = 0 \qquad (73)$$

for all lengths $L > 0$. However, $W(L)$ becomes infinite for $L = 0$ if $\eta \to +0$, i.e. $W(L)$ becomes a delta-function centred in $L = 0$. (In fact, we ought to speak of one half of the delta-function, as we do not consider negative values of L.)

The final item that we will now discuss is the calculation of the dispersion (variance) of the perpendicular component $\vec{\Omega}_\perp$ of the tangential unit vector $\vec{\Omega}$. We define this dispersion by the integral

$$[\sigma^\perp_{\rm ang}(L)]^2 = \int \mathrm{d}^2\Omega\; \vec{\Omega}^{\,2}_\perp\; \tilde{P}^{\rm c}_{\rm ang}(\vartheta, L) = 2\pi \int_0^\pi \mathrm{d}\vartheta\; \sin\vartheta \sin^2\vartheta\; \tilde{P}^{\rm c}_{\rm ang}(\vartheta, L)$$

$$= 2\pi \int_0^\pi \mathrm{d}\vartheta\, \sin\vartheta\, (1-\cos^2\vartheta)\, \tilde{P}^{\rm c}_{\rm ang}(\vartheta, L) = 1 - 2\pi \int_0^\pi \mathrm{d}\vartheta\, \sin\vartheta \cos^2\vartheta\, \tilde{P}^{\rm c}_{\rm ang}(\vartheta, L)\;. \quad (74)$$

We can do the integration as follows:

$$\int_0^\pi \mathrm{d}\vartheta\; \sin\vartheta \cos^2\!\vartheta\; \exp(C\cos\vartheta) = \frac{\mathrm{d}^2}{\mathrm{d}C^2} \int_0^\pi \mathrm{d}\vartheta\; \sin\vartheta\; \exp(C\cos\vartheta)$$

$$= \frac{\mathrm{d}^2}{\mathrm{d}C^2}\, \frac{\sinh C}{C} = \frac{\sinh C}{C} - \frac{2}{C^2}\left(\cosh C - \frac{\sinh C}{C}\right). \quad (75)$$

Thereupon,

$$[\sigma^\perp_{\rm ang}(L)]^2 = 2\, \frac{\sinh(KL)}{\beta\eta K} \left[\mathrm{cotanh}\left(\frac{\beta\eta K}{\sinh(KL)}\right) - \frac{\sinh(KL)}{\beta\eta K}\right]$$

$$= 2\, \frac{\sinh(KL)}{\beta\eta K}\, W(L)\,, \quad (76)$$

or,

$$[\sigma^\perp_{\rm ang}(L)]^2 = 2\sqrt{\frac{\lambda}{3\beta\eta}}\, \sinh\!\left(\sqrt{\frac{3}{\lambda\beta\eta}}\, L\right) \sinh\!\left(\sqrt{\frac{3\beta\eta}{\lambda}} \Big/ \sinh\!\left(\sqrt{\frac{3}{\lambda\beta\eta}}\, L\right)\right) W(L) \quad (77)$$

with $W(L)$ given by expression (71).

Let us now discuss the particular case when $KL \ll 1$. Then the dispersion $[\sigma^\perp_{\rm ang}(L)]^2$ becomes simplified:

$$[\sigma^\perp_{\rm ang}(L)]^2 \approx \frac{2L}{\beta\eta} = \frac{2k_{\rm B}TL}{\eta} \quad (78)$$

for

$$\eta \gg \frac{3L^2}{\lambda\beta} = \frac{3k_{\rm B}TL^2}{\lambda}\,. \quad (79)$$

Moreover, since $L \gg \lambda$, condition (80) implies also the condition

$$\eta \gg \frac{2L}{\beta} = 2k_{\rm B}TL\,, \quad (80)$$

so that we may state that

$$[\sigma^\perp_{\rm ang}(L)]^2 \ll 1 \quad (81)$$

in this case. Under condition (80), the polymers behave like very stiff, but still elastic, thin rods. In analogy to the definition of 'paraxial rays' in optics, we may say that condition (80) defines the *paraxial approximation* in the theory of polymer configurations. In this approximation, $0 \le \vartheta \ll 1$, so we may accept the equalities

$$\vec{\Omega}.\vec{\Omega}_0 \approx 1 - \frac{\vartheta^2}{2}, \tag{82}$$

$$\sin\vartheta \approx \vartheta . \tag{83}$$

Under condition (80), we may also employ the approximation

$$\sinh\left(\frac{\beta\eta K}{\sinh(KL)}\right) \approx \sinh\left(\frac{\beta\eta}{L}\right) \approx \frac{1}{2}\exp\left(\frac{\beta\eta}{L}\right). \tag{84}$$

Then the probability density $\tilde{P}^{\mathrm{c}}_{\mathrm{ang}}(\vartheta, L)$ (cf. expression (66)) goes over into a Gaussian in the variable ϑ:

$$\tilde{P}^{\mathrm{c}}_{\mathrm{ang}}(\vartheta, L) \approx \tilde{P}^{\mathrm{c}}_{\mathrm{parax}}(\vartheta, L) = \frac{1}{2\pi}\frac{\beta\eta}{L}\exp\left(-\frac{\beta\eta}{2L}\vartheta^2\right), \quad \vartheta \ge 0 . \tag{85}$$

[The prefactor $1/(2\pi)$ is due to the fact that, when integrating the function $\tilde{P}^{\mathrm{c}}_{\mathrm{ang}}(\vartheta, L)$ with respect to $\vec{\Omega}$, we have to perform the integration with respect to the angle φ (even if $\tilde{P}^{\mathrm{c}}_{\mathrm{ang}}(\vartheta, L)$ does not depend on φ).]

In the paraxial approximation, it is easy to calculate any statistical moment of the random variable ϑ. In particular, when using equality (84), we can calculate the second statistical moment of ϑ as follows:

$$\langle\vartheta^2\rangle = 2\pi\int_0^\infty \mathrm{d}\vartheta\,\vartheta^3\,\tilde{P}^{\mathrm{c}}_{\mathrm{ang}}(\vartheta, L) = \frac{\beta\eta}{L}\int \mathrm{d}\vartheta\,\vartheta^3\,\exp\left(-\frac{\beta\eta}{2L}\vartheta^2\right) = \frac{2L}{\beta\eta}. \tag{86}$$

This is in full agreement with formula (79).

4 Concluding remarks

The main goal of the present paper was the exact derivation of the end-to-end probability density $P^{\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$ (formula (50)). With this function, as we have shown in Section 3, exacting calculations can be accomplished, such as the calculation of the mean-square end-to-end distance $\langle R^2\rangle_L$ or the dispersion $[\sigma^{\perp}_{\mathrm{ang}}(L)]^2$ of the projection of the tangential random unit vector $\vec{\Omega}$, corresponding to one of the polymer ends, onto the plane perpendicular to the given tangential direction of the opposite end (i.e. onto the plane perpendicular to $\vec{\Omega}_0$). The calculation of the quantities $\langle R^2\rangle_L$ and $[\sigma^{\perp}_{\mathrm{ang}}(L)]^2$ – see especially formulae (60), (70) and (77)) gives us a cogent argument to believe that the function $P^{\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$ may be very adequate even for calculations of other mean values occurring in the polymer theory.

However, we must stress one point. The constraint $|\mathbf{v}(L)| = 1$ with which we have defined the probability density $P^{\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$ implies one general consequence: when accepting this constraint, we have actually refrained from the Markovian property of the random chain of the monomers forming the polymer. Instead, we have to say that the arrangement of the monomers manifests a 'memory' if the stiffness parameter η is not equal to zero. Therefore, if $\eta > 0$,

$$P^{\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0) \neq$$

$$\int \mathrm{d}^3 r_1 \int \mathrm{d}^2 \Omega_1 \, P^{\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L_1|\mathbf{r}_1, \vec{\Omega}_1) \, P^{\mathrm{c}}(\mathbf{r}_1, \vec{\Omega}_1, L - L_1|\mathbf{r}_0, \vec{\Omega}_0) \,. \tag{87}$$

(The Markovian property would require that this inequality should be changed into equality for each value of L_1, $0 \le L_1 \le L$. Let us point out that the equality of the r.h. side in (88) with $P^{\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$ has been spoilt by the angular integration.) Inequality (88) is contrasting with the equality

$$G(\mathbf{r}, \mathbf{v}, L|\mathbf{r}_0, \mathbf{v}_0) = \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 v_1 \, G(\mathbf{r}, \mathbf{v}, L_1|\mathbf{r}_1, \mathbf{v}_1) \, G(\mathbf{r}_1, \mathbf{v}_1, L - L_1|\mathbf{r}_0, \mathbf{v}_0) \tag{88}$$

stemming from the very definition of Green's function (18) by the path integral (19). Thus, we may state that $P^{\mathrm{c}}(\mathbf{r}, \vec{\Omega}, L|\mathbf{r}_0, \vec{\Omega}_0)$ corresponds to a non-Markovian process in a 5-dimensional space but this process has got its origin in the Markovian process described by the function $G(\mathbf{r}, \mathbf{v}, L|\mathbf{r}_0, \mathbf{v}_0)$ in the 6-dimensional space $\{\mathbf{r}, \mathbf{v}\}$.

There are many basic questions in the theory of polymers that have not been answered sufficiently yet. Some of these questions have been notorious to investigators in the field with the label 'very difficult'. Such is, for instance, the question of the behaviour of polymers when they are intertwined with one another, forming possibly a statistical system of randomly distributed cross-links. (Undeniably this takes place in rubbers.) We can also mention the difficult topic of topological constraints, the exclusion-volume problem, etc.

In their review papers, Edwards and Freed (cf. [1], [2]), presented a lucid particularization of problems occurring in the statistical theory of polymers on 'simpler' and 'difficult' ones. We agree with the viewpoints of these authors and so we must admit that what we have described in the present paper belongs undoubtedly to the category of the 'simpler' problems. Some of these problems, fortunately, proved to be exactly solvable. The 'difficult' problems, on the other hand, hardly may be termed as 'exactly solvable' in the classical style of the theoretical physics. To resolve them satisfactorily, we do not see any other way than to use ultrafast computers enabling specialists to implement adequate multivariable Monte Carlo procedures. Nevertheless, many theorists believe − and we share this belief − that a reliable resolution of the 'simpler' problems can yield bricks which may eventually become usable in formulating efficient computing programmes for solving the 'difficult' problems. In this context, let us cite Freed [1]: "... a box full of cross-linked polymers (a rubber) is a box full of Feynman diagrams! Here the abstraction becomes reality."

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