PHYSICAL REVIEW E VOLUME 54, NUMBER 3 SEPTEMBER 1996

Kramers equation as a model for semiflexible polymers

Semjon Stepanow
Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik, D-06099 Halle/Saale, Germany

(Received 27 March 1996)

We propose to use the Kramers equation for a Brownian particle diffusing in phase space as a model to describe semiflexible polymer chains. [S1063-651X(96)50608-2]

PACS number(s): 36.20.−r, 05.40.+j

The analogy between the description of flexible polymer chains, random walks, the theory of Brownian motion, and quantum mechanics enables one to apply the methods developed in the theory of diffusion processes, quantum mechanics, and quantum field theory such as path integrals, perturbation expansions, and renormalization group to polymer physics [1,2]. The Edwards model [3] of a flexible polymer chain, which influenced to a great extent the modern development of polymer physics, can be considered in some sense as a minimal model for flexible polymers: it describes correctly the essential properties of the polymer chain on large scales and imposes minimal restrictions on microscopic lengths. However, there is a large class of polymers that cannot be considered as flexible. Semiflexible polymers play an important role in various applications such as liquid crystalline polymers, biopolymers, etc. Semiflexible polymers are usually described by using the Kratky-Porod model [4,5]. Although the latter permits an exact consideration (see, for example, [6,7]) for a free chain, the computation of different quantities already becomes a difficult task for a free polymer chain. Therefore, it is relevant to look for a more simple model for semiflexible polymers reproducing on large scales the essential properties of semiflexible polymers and imposing on small scales less restrictions than the Kratky-Porod model. The weakening of restrictions on small scales is expected to result in a simplified model, which is especially desirable for chains with interactions.

The aim of this Rapid Communication is to propose a model for semiflexible polymers based on the extension of the analogy between the theory of Brownian motion and polymer statistics. The main idea is very simple and is based on the following observation. From the theory of Brownian motion it is known that in contrast to the Smoluchowski equation (Fokker-Planck equation without inertia), the Kramers equation (Fokker-Planck equation with inertia) possesses a ballistic regime for small times (see [8] or, for example, the textbook [9]). This is due to the fact that the Kramers equation includes the velocity of the Brownian particle as a dynamical variable, so that for sufficiently small times, where the effect of friction is small, this equation possesses a ballistic regime. It is tempting to interpret this ballistic regime in terms of polymer chains as the stiffness of the latter. It appears that the correlation functions for the velocity and the space coordinate of the particle [see Eqs. (12,13)] coincide exactly with the correlation functions of the tangent and monomer coordinates of the Kratky-Porod polymer chain. In contrast to the Kratky-Porod chain, where the tangent at the arbitrary point of the polymer is fixed, the velocity of the Brownian particle is a fluctuating quantity. Thus, the Kramers formalism reproduces the essential property of the polymer chain on large scales and imposes less restrictions than the Kratky-Porod model on small scales.

We start with the Kramers equation of the particle in the absence of an external force as considered by Uhlenbeck and Ornstein [10]. The probability density $w(\mathbf{r},\mathbf{v},t)$ obeys the equation [11]

$$\frac{\partial w(\mathbf{r},\mathbf{v},t)}{\partial t}=\frac{\partial}{\partial \mathbf{v}}\left(\gamma \mathbf{v} w+D_v \frac{\partial}{\partial \mathbf{v}} w\right)-\mathbf{v}\frac{\partial}{\partial \mathbf{r}} w, \tag{1}$$

where $\mathbf{v}$ is the velocity, $\mathbf{r}$ denotes the position of the particle, $D_v=\gamma k T m^{-1}$ is the diffusion coefficient in the velocity space, γ is the friction coefficient, and m is the mass of the particle. The velocity variable in Eq. (1) satisfies the Langevin equation

$$m\frac{d\mathbf{v}}{dt}=-\gamma\mathbf{v}+\mathbf{f}(t), \tag{2}$$

where the noise force $\mathbf{f}(t)$ is Gaussian distributed and is characterized by the correlation function

$$\langle f_\mu(t) f_\nu(t')\rangle=\delta_{\mu\nu}2D_v\delta(t-t').$$

The variables $\mathbf{r},\mathbf{v}\equiv\xi$ form the μ space. By using the ξ variable Eq. (1) can be rewritten as

$$\frac{\partial w}{\partial t}=\sum_{\nu=1}^{6}\frac{\partial(A_\nu w)}{\partial \xi_\nu}+\sum_{\nu,\mu=1}^{6} D_{\mu\nu}\frac{\partial^2 w}{\partial\xi_\nu\partial\xi_\mu}, \tag{3}$$

where $A_\nu=(-\mathbf{v},\gamma\mathbf{v})$ and $D_{\mu\nu}=D_v\delta_{\mu\nu}\theta(\mu-3)$ with $\theta(x)$ being the step function. Equation (3) now has the form of the Smoluchowski equation. The representation of the latter by using path integrals is straightforward [12]. The transition probability $P_0(\mathbf{r},\mathbf{v},\Delta t+t;\mathbf{r}_0,\mathbf{v}_0,t)$ from the point $\mathbf{r}_0,\mathbf{v}_0$ at time t to the point $\mathbf{r},\mathbf{v}$ at time $t+\Delta t$ for an infinitesimal time interval Δt is given by

$$\begin{aligned}P_0(\mathbf{r},\mathbf{v},\Delta t+t;\mathbf{r}_0,\mathbf{v}_0,t)\\ =\frac{1}{(4\pi D_v\Delta t)^{d/2}}\delta(\mathbf{r}-\mathbf{r}_0-\Delta t\mathbf{v}_0)\\ \times\exp\left(-\frac{1}{4D_v\Delta t}(\mathbf{v}-\mathbf{v}_0+\Delta t\gamma\mathbf{v}_0)^2\right).\end{aligned} \tag{4}$$

In order to get the representation of the transition probability for a finite time interval as a path integral we divide the interval $[0,t]$ in n infinitesimal intervals of the width $\Delta t = t/n$, use the Markovian property of the transition probability

$$P_0(\mathbf{r},\mathbf{v},t;\mathbf{r}_0,\mathbf{v}_0,0) = \int d\mathbf{r}' \int d\mathbf{v}' P_0(\mathbf{r},\mathbf{v},t;\mathbf{r}',\mathbf{v}',t') \times P_0(\mathbf{r}',\mathbf{v}',t';\mathbf{r}_0,\mathbf{v}_0,0) \tag{5}$$

$(t' \in [0,t])$ $n-1$ times and get in the limit $n \to \infty$

$$P_0(\mathbf{r},\mathbf{v},t;\mathbf{r}_0,\mathbf{v}_0,0) = \int_{\mathbf{r}(0)=\mathbf{r}_0,d\mathbf{r}(0)/dt=\mathbf{v}_0}^{\mathbf{r}(t)=\mathbf{r},d\mathbf{r}(t)/dt=\mathbf{v}} D\mathbf{r}(t) \times \exp\left[-\frac{1}{4D_v}\int_0^t dt' \left(\frac{d^2\mathbf{r}}{dt'^2} + \gamma \frac{d\mathbf{r}}{dt'} \right)^2 \right]. \tag{6}$$

The form of the measure in Eq. (6) is evident from Eq. (4). The evaluation of the path integral can be performed by using the method of steepest descents. This results in

$$P_0(\mathbf{r},\mathbf{v},t;\mathbf{r}_0,\mathbf{v}_0,0) = \left(\frac{\gamma}{2\pi D_v[1-\exp(-2\gamma t)]} \right)^{d/2} \left(\frac{\gamma^3}{4\pi D_v} \frac{1+\exp(-\gamma t)}{\gamma t - 2 + \gamma t \exp(-\gamma t) + 2\exp(-\gamma t)} \right)^{d/2}$$
$$\times \exp\left[-\frac{\gamma}{2D_v[1-\exp(-2\gamma t)]} [\mathbf{v} - \mathbf{v}_0 \exp(-\gamma t)]^2 - \frac{\gamma^3}{4D_v} \frac{1+\exp(-\gamma t)}{\gamma t - 2 + \gamma t \exp(-\gamma t) + 2\exp(-\gamma t)} \left(\mathbf{r} - \mathbf{r}_0 + \gamma^{-1} \frac{1-\exp(-\gamma t)}{1+\exp(-\gamma t)} (\mathbf{v} + \mathbf{v}_0) \right)^2 \right]. \tag{7}$$

The Fourier transform of the transition probability $P_0(\mathbf{r},\mathbf{v},t;\mathbf{r}_0,\mathbf{v}_0,0)$, which we will give for reference, is obtained from Eq. (7) as

$$P_0(\mathbf{p},\mathbf{k},\mathbf{k}',t) = \delta\left(\mathbf{k}' - \mathbf{k}e^{-\gamma t} - \mathbf{p}\frac{1-e^{-\gamma t}}{\gamma} \right) \times \exp\left(-\frac{D_v p^2}{2\gamma^3}[2\gamma t + 4e^{-\gamma t} - e^{-2\gamma t} - 3] - \frac{D_v k^2}{2\gamma}(1-e^{-2\gamma t}) - \frac{D_v \mathbf{p}\cdot\mathbf{k}}{\gamma^2}(1-e^{-\gamma t})^2 \right), \tag{8}$$

where the variables $\mathbf{p}$, $\mathbf{k}$, and $\mathbf{k}'$ are respectively conjugated to $\mathbf{r}-\mathbf{r}_0$, $\mathbf{v}$, and $-\mathbf{v}_0$.

The mean square velocity and the mean square displacement of the particle are directly computed from Eqs. (7) or (8) as

$$\langle \mathbf{v}^2(t) \rangle|_{\mathbf{v}_0} = \frac{dD_v}{\gamma}[1-\exp(-2\gamma t)] + \mathbf{v}_0^2 \exp(-2\gamma t), \tag{9}$$

$$\langle (\mathbf{r}(t)-\mathbf{r}_0)^2 \rangle|_{\mathbf{v}_0} = \frac{dD_v}{\gamma^3}(2\gamma t + 4e^{-\gamma t} - e^{-2\gamma t} - 3) + \frac{\mathbf{v}_0^2}{\gamma^2}(1-e^{-\gamma t})^2. \tag{10}$$

Equations (9,10) were first derived by Uhlenbeck and Ornstein [10] (see also Chandrasekhar [8]). For large t the mean square of the velocity is independent of $\mathbf{v}_0$ and becomes

$$\langle \mathbf{v}^2(t) \rangle = \frac{dD_v}{\gamma}. \tag{11}$$

The correlation function of the velocity is obtained by using Eq. (7) and performing the average over $\mathbf{v}_0$ with help of the Maxwell distribution, $P_0(\mathbf{v}) \sim \exp[-(d/2)\mathbf{v}_0^2]$, as

$$\langle \mathbf{v}(t_2)\mathbf{v}(t_1) \rangle = \frac{dD_v}{\gamma}\exp(-\gamma|t_2-t_1|), \tag{12}$$

where t_1, $t_2 \in (0,t)$. The latter can be used to compute the correlation function $\langle [\mathbf{r}(t_2)-\mathbf{r}(t_1)]^2 \rangle$. The result is

$$\langle [r(t_2)-\mathbf{r}(t_1)]^2 \rangle = \frac{dD_v}{\gamma}\frac{2}{\gamma}\left(|t_2-t_1| + \frac{1}{\gamma}\exp(-\gamma|t_2-t_1|) - \frac{1}{\gamma} \right). \tag{13}$$

Equations (12,13) can be obtained from Eqs. (9,10) by setting $\mathbf{v}_0^2$ by its mean value given by Eq. (11). The results (12,13) were first derived by Uhlenbeck and Ornstein [10] (see also [8]).

There are two independent parameters D_v and γ in the Kramers equation. In order to use the Kramers equation to describe a polymer chain we fix D_v according to $dD_v/\gamma = dkT/m = 1$. The time t will be identified with the coordinate s along the contour of the polymer chain. The Kramers equation for the polymer chain is obtained from (1) by replacing t through s and $D_v = \gamma/d$. Equations (12,13) expressed in terms of the polymer quantities read

$$\langle \mathbf{v}(s+s_0)\mathbf{v}(s_0) \rangle = \exp(-s/l_p), \tag{14}$$

$$\langle [\mathbf{r}(s+s_0)-\mathbf{r}(s_0)]^2 \rangle = 2l_p[s + l_p\exp(-s/l_p) - l_p], \tag{15}$$

where $l_p \equiv \gamma^{-1}$ is the persistence length of the polymer chain. Equations (14,15) coincide exactly with the results obtained by using the Kratky-Porod model [6]. Despite the fact that the tangent of the polymer chain in the present model is not constant and fluctuates with the mean square value obeying the condition $\langle \mathbf{v}^2\rangle = 1$, the statistical properties of both the Kratky-Porod model and the Kramers model expressed by correlation functions (14,15) are the same. Thus, the Kramers model describes the essential properties of the semiflexible polymers on large scales, but in contrast to the Kratky-Porod chain, the former imposes less restrictions on small scales. This circumstance results in a simplification of the tractability of the model.

The statistical weight $P_0(\mathbf{r},\mathbf{v},L;\mathbf{r}_0,\mathbf{v}_0,0)$ associated with the configuration $r(s)$ $(0 \leqslant s \leqslant L)$ of the polymer chain is obtained from Eq. (6) as a path integral as

$$P_0(\mathbf{r},\mathbf{v},L;\mathbf{r}_0,\mathbf{v}_0,0)=\int_{\mathbf{r}(0)=\mathbf{r}_0,d\mathbf{r}(s)/ds|_{s=0}=\mathbf{v}_0}^{\mathbf{r}(L)=\mathbf{r},d\mathbf{r}(L)/dL=\mathbf{v}} D\mathbf{r}(s) \times\exp\left[-\frac{d}{4}l_p\int_0^L ds\left(\frac{d^2\mathbf{r}}{ds^2}+l_p^{-1}\frac{d\mathbf{r}}{ds}\right)^2\right]. \tag{16}$$

So far, we have considered the case of a free polymer chain. In this case $P_0(\mathbf{r},\mathbf{v},L;\mathbf{r}_0,\mathbf{v}_0,0)$ is a probability density for $\mathbf{r}$ and $\mathbf{v}$ and is normalized to one. In contrast to the Brownian particle, the polymer segments couple to the external potential and not to the force. Consequently, in order to describe a polymer chain in an external field, the interaction energy, $U_{int}=\int_0^L ds U[\mathbf{r}(s),d\mathbf{r}(s)/ds]$, should be added (multiplied with -1) to the exponential of Eq. (16). The consequence of this coupling is that Eq. (16) is not more normalized and we have to interpret the integrand on the right-hand side of Eq. (16) as a statistical weight for a configuration $\mathbf{r}(s)$. For both free polymer chains and chains with interaction the average over $\mathbf{v}_0$ has to be performed with the help of the equilibrium distribution function of the velocity.

To conclude, we have extended the analogy between the theory of Brownian motion and the statistics of polymer chains and have proposed to describe the semiflexible polymer chains by using the Kramers equation. It seems that the model based on the Kramers equation gives a minimal model to describe semiflexible polymers: it describes essential properties of the semiflexible polymers and possesses less restrictions in comparison to the Kratky-Porod model. The possibility of treatment of the Kramers equation by using field theoretic methods such as path integrals, perturbation expansions, etc. gives hope that the Kramers model will be convenient for treating complicated systems of semiflexible polymers such as polyelectrolytes, blends of semiflexible polymers, etc.

I acknowledge stimulating discussions with Y. Rabin, S. Alexander, S. Havlin, K. Kremer, T. A. Vilgis, U. Bauerschäfer, and S. Trimper. I also acknowledge the hospitality of the Bar-Ilan University, Ramat-Gan, Israel. I acknowledge partial support from the Deutsche Forschungsgemeinschaft (Contract No. SFB 1575).

---

[1] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
[2] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Press, Ithaca, 1979).
[3] S. F. Edwards, Proc. Phys. Soc. London **85,** 613 (1965).
[4] O. Kratky and G. Porod, Recl. Trav. Chim. Pays-Bas **68,** 1106 (1949).
[5] K. F. Freed, Adv. Chem. Phys. **22,** 1 (1972).
[6] J. Des Cloizeaux, and G. Jannink, *Polymers in Solution, Their Modelling and Structure* (Clarendon Press, Oxford, 1990).
[7] M. Otto, J. Jäkert, and T. A. Vilgis, Macromol. Theory Simul. **3,** 543 (1994).
[8] S. Chandrasekhar, Rev. Mod. Phys. **15,** 1 (1943).
[9] Yu. L. Klimontovich, *Statistical Physics* (Nauka, Moscow, 1982).
[10] Y. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36,** 1823 (1930).
[11] H. A. Kramers, Physica (Amsterdam) **7,** 284 (1940).
[12] F. Langouche, D. Roekaerts, and E. Tirapegui, Physica A **97,** 195 (1979).