Advanced Studies in Theoretical Physics
Vol. 9, 2015, no. 1, 1 - 11
HIKARI Ltd, www.m-hikari.com
http://dx.doi.org/10.12988/astp.2015.411148

First-Principles Calculations of Internal Friction of a Gaussian Chain

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Abstract

We consider internal friction of a Gaussian chain placed in vacuum. Dynamics of a single chain can be described by Langevin equation where the random force term comes from the random collisions of monomers among themselves. To find the moment of these random forces, Gaussian distribution for chain conformation is used . Since collisions between monomers cause these forces, random forces on two monomers can be equal and opposite at the same time. Such correlation is exploited to find friction constant ζ for Fourier mode p. We show that this same mechanism of internal friction is also applicable for polymers in solution.

PACS: 47.57.Ng; 05.40.Jc; 83.10.Mj

Keywords: internal friction, Gaussian distribution, Langevin equation, Oseen tensor

1 Introduction

Any dissipative mechanism that does not involve solvent is referred as internal friction in polymer physics [1], [2], [3], [4]. Some recent advancements have renewed interest in this long standing problem. Ionization techniques such as

MALDI(Matrix assisted laser desorption/ionization)[5] or electrospray ionization [6] has made it possible to get large polymers in gases or vacuum. Since friction constant is much smaller in this media, internal friction will have a significant impact on the dynamics of polymer in gases. Also it would be possible to measure internal friction effect directly and to check the validity of extrapolation scheme so far used for polymers in solution.

Dynamics of a polymer in vacuum has been considered theoretically [7], [8], [9]. Also internal friction term of a polymer in vacuum has been studied by computer simulation [10]. This friction is quite similar to that of Kelvin friction. If by $\mathbf{R}_n$ we denote the position of monomer n, Kelvin friction term is proportional to $\frac{\partial}{\partial t}(\frac{\partial^2 \mathbf{R}_n}{\partial n^2})$. This term says how the bond angle is changing with time. So this friction basically results in from the interaction between neighbouring monomers. But polymer is an one dimensional object placed in 3D. Monomers distant along the chain may come close in space and make random collisions. For ideal chain, number of monomers involved in such random collisions can be quite large [11]. In this paper, we will consider internal friction that comes from random collisions between monomers distant along the chain. Effect of this friction would be much stronger than Kelvin damping. This type of frictional process had been considered by P.G. de Gennes [2]. He made the assumption that friction on monomer n by monomer m is proportional to their relative velocity and total friction on monomer n can be obtained by taking sum over all other monomers. In essence, it's a phenomenological theory. Recent improvements as mentioned in the introduction necessitates a first-principles calculation of this internal friction. At first we will calculate internal friction in vacuum and at the end we will show that this mechanism is applicable in solution as well.

2 Derivation of internal friction constant ζ_p

We propose that in vacuum, equation of motion of a single chain can be described by Langevin equation [12]

$$\zeta \frac{\partial \mathbf{R}_n}{\partial t} = k \frac{\partial^2 \mathbf{R}_n}{\partial n^2} + \mathbf{f}_n, \tag{1}$$

where $\mathbf{R}_n$ is the position of monomer n, $k = \frac{3k_B T}{b^2}$ [13] and $\mathbf{f}_n$ is the random force on monomer n due to its collisions with other monomers as shown in figure (1). The friction constant ζ is related to the mean square momentum transfer to a monomer by random collisions, and only other monomers are involved in these random collisions. The value of ζ will be determined and subsequently used to solve equation (1) in terms of normal modes.

We will assume that at temperature T, monomers will follow Maxwell's momentum distribution. To determine the internal friction for a Gaussian

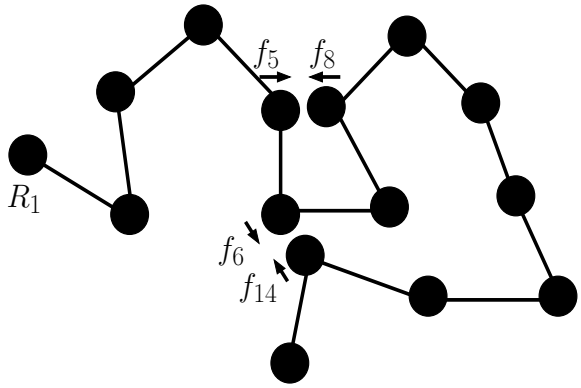

Figure 1: Monomers distant along the chain undergo random collisions. Random forces on a pair of monomers can be treated as equal and opposite. Here $\mathbf{f}_5 = -\mathbf{f}_8$ and $\mathbf{f}_6 = -\mathbf{f}_{14}$.

chain, the Gaussian distribution for conformations will be used to find the number of monomers at a given distance. First let us find the mean square momentum transfer in these collisions.

We will consider the monomers as hard spheres and the collisions they make are elastic. If two monomers collide, the angle of deflection in the center of mass reference frame is given by [14]

$$\chi(b_{im}, g) = \pi - 2b_{im} \int_{r_m}^{\infty} \frac{\frac{dr}{r^2}}{\sqrt{1 - \frac{\varphi(r)}{\frac{1}{2}\mu g^2} - \frac{b_{im}^2}{r^2}}},$$

where b_{im} is the impact parameter, $\varphi(r)$ is the interaction potential, μ is the reduced mass, and g is the initial relative speed.

If R is the radius of hard sphere, r_m would be $2R$ for impact parameter less than $2R$ and $\varphi(r) = 0$ within the range of integration. So $\chi(b_{im}) = \pi - 2b_{im} \int_{2R}^{\infty} \frac{\frac{dr}{r^2}}{\sqrt{1-\frac{b_{im}^2}{r^2}}} = \pi - 2\sin^{-1}\left(\frac{b_{im}}{2R}\right)$. Setting v be the speed of one sphere in the laboratory reference frame and, with the other sphere at rest in this frame. If ψ is the deflection angle for the sphere which is moving with velocity v in laboratory reference frame and ξ is the deflection angle for sphere at rest, then $\psi + \xi = \frac{\pi}{2}$. Also for equal mass, $\psi = \frac{\chi}{2}$. This gives $\xi = \sin^{-1}\left(\frac{b_{im}}{2R}\right)$. After the collision, the sphere which was at rest acquires speed v' in the laboratory frame, and from momentum conservation we will find $v' = \frac{v}{(\sin\xi\cot\psi + \cos\xi)} = v\sqrt{1 - \left(\frac{b_{im}}{2R}\right)^2}$. Thus, when a sphere with momentum p collides with a sphere at rest, the momentum transfer for the impact parameter b_{im} is $p\sqrt{1 - \left(\frac{b_{im}}{2R}\right)^2}$.

Now we want to know the mean square momentum transfer $\langle p'^2 \rangle$. Monomers can collide with any impact parameter and can have any velocity. Therefore, we will average over all impact parameters and incoming momentums:

$$\begin{aligned}\langle p'^2 \rangle &= \frac{\int\int p^2(1-(\frac{b_{im}}{2R})^2)f(p)db_{im}dp}{\int db_{im}\int f(p)dp} \\ &= 2mk_BT.\end{aligned}$$

It is now necessary to evaluate the number of collisions a given monomer will have per unit time. If $P(2R)$ is the monomer number density at a distance $2R$ from the center of a given monomer, the average number of collisions this monomer will make per unit time is $\langle \frac{d\Gamma}{dt} \rangle = 4\pi(2R)^2 \bar{v_\perp} P(2R)$. Here we will use $\bar{v_\perp} = \frac{\int_0^\infty dvv \exp^{-\frac{mv^2}{2k_BT}}}{\int_{-\infty}^\infty \exp^{-\frac{mv^2}{2k_BT}}}$, and the distribution of conformations for an ideal chain for P(2R). As with the end-to-end radius, the distance between any two points of an ideal chain follows a Gaussian distribution [15]. So

$$\begin{aligned}P(2R) &= \sum_{n=1}^{N}\left(\frac{3}{2\pi n b^2}\right)^{\frac{3}{2}} e^{-\frac{3(2R)^2}{2nb^2}} \\ &= \left(\frac{3}{2\pi b^2}\right)^{\frac{3}{2}} \sum_{p=0}(-1)^p \left(\frac{6R^2}{b^2}\right)^p . \left(\frac{1}{p!}\right) \sum_{n=1}^{N} \frac{1}{n^{p+\frac{3}{2}}}.\end{aligned}$$

For $N \to \infty$,

$$\begin{aligned}P(2R) &= \left(\frac{3}{2\pi b^2}\right)^{\frac{3}{2}} \sum_{p=0}(-1)^p \frac{1}{p+\frac{1}{2}} \left(6(\frac{R}{b})^2\right)^p \\ &\approx (\frac{3}{2^{\frac{1}{3}}\pi})^{\frac{3}{2}} \frac{1}{b^3} + \frac{1}{b^3} O\left((\frac{R}{b})^2\right).\end{aligned}$$

Thus, the mean square momentum transfer per second is

$$\langle p'^2 \rangle \langle \frac{d\Gamma}{dt} \rangle = \frac{(3^{\frac{3}{2}})(4)}{\pi} (k_BT)^{\frac{3}{2}} \sqrt{m} \left(\frac{R^2}{b^3}\right). \tag{2}$$

Since $\langle f(t)f(0) \rangle = 2\zeta k_BT\delta(t)$, above equation gives $\zeta = (\frac{(2)(3^{\frac{3}{2}})}{\pi})(\frac{R^2}{b^3})(mk_BT)^{\frac{1}{2}}$.

To solve equation (1), the normal components of random forces are given by

$$\mathbf{f}_p = \frac{1}{\sqrt{N}} \int dn \cos(\frac{p\pi n}{N}) \mathbf{f}_n. \tag{3}$$

If monomers n and n' collide, random forces on these two monomers will be equal and opposite. Since all the random force terms on the right side of equation (3) come as pairs, the presence of any term (for example $\mathbf{f}_1$) immediately

implies that there is another term equal to $-\mathbf{f}_1$. This is a very important fact, and determines what values of $\mathbf{f}_p$ are allowed. We want to find relaxation τ_p which is proportional to $\frac{\zeta_p}{k_p}$. Here k_p is the property of the Gaussian chain and does not change unless the temperature changes. But the term ζ_p will be different if the random forces come as pairs. This imposes restrictions on the dissipative mechanism and these are central to the remaining derivations.

We have to consider all the possible collisions with probability $P_{nn'}$, i.e., probability that monomer n' will collide with n. We will assume that two monomers will collide only when they are at the same point and we know this probability from the properties of Gaussian chain. Since $\mathbf{f}_n = -\mathbf{f}'_n$, one term in the summation for $\mathbf{f}_p$ will be proportional to $\left(\cos(\frac{p\pi n}{N}) - \cos(\frac{p\pi n'}{N})\right)$. So the time correlation of $\mathbf{f}_p$ and $\mathbf{f}_q$ will be

$$\langle \mathbf{f}_p(t) \cdot \mathbf{f}_q(0) \rangle = \frac{1}{N} \int\int dn dn' P_{nn'} \left[\cos\left(\frac{p\pi n}{N}\right) - \cos\left(\frac{p\pi n'}{N}\right) \right] \left[\cos\left(\frac{q\pi n}{N}\right) - \cos\left(\frac{q\pi n'}{N}\right) \right] \langle \mathbf{f}_n(t) \cdot \mathbf{f}_n(0) \rangle.$$

Here $\langle \mathbf{f}_n(t) \cdot \mathbf{f}_n(0) \rangle$ is related to the mean square momentum transfer, i.e., $\langle \mathbf{f}_n(t) \cdot \mathbf{f}_n(0) \rangle = \langle p'^2 \rangle \langle \frac{d\Gamma}{dt} \rangle \delta(t)$, and $P_{nn'}$ is the probability of two monomers n and n' being at the same point. Thus,

$$\langle \mathbf{f}_p(t) \cdot \mathbf{f}_q(0) \rangle = \frac{4}{N} \langle p'^2 \rangle \langle \frac{d\Gamma}{dt} \rangle \delta(t) \int\int dn dn' \left\{ \frac{\sin\left(\frac{p\pi(n-n')}{2N}\right) \sin\left(\frac{q\pi(n-n')}{2N}\right)}{|n-n'|^{\frac{3}{2}}} \right\} \left\{ \sin\left(\frac{p\pi(n+n')}{2N}\right) \sin\left(\frac{q\pi(n+n')}{2N}\right) \right\}. \tag{4}$$

Consider the summation

$$I(p,q) = \sum_{\substack{n,n' \\ n \neq n'}} \left[\frac{\sin\left(p'(n-n')\right) \sin\left(q'(n-n')\right)}{|n-n'|^{\frac{3}{2}}} \right] \left[sin\left(p'(n+n')\right) \sin\left(q'(n+n')\right) \right],$$

where we have used the notation $p' = \frac{p\pi}{2N}$ and $q' = \frac{q\pi}{2N}$. To perform the summation we will make a change in coordinates:

$$u = n - n',$$
$$v = n + n'.$$

This will give:

$$I(p,q) = \sum_{u=1}^{N} \frac{\sin(p'u)\sin(q'u)}{|u|^{\frac{3}{2}}} \sum_{v=u}^{2N-u} \sin(p'v)\sin(q'v) + \sum_{u=-N}^{-1} \frac{\sin(p'u)\sin(q'u)}{|u|^{\frac{3}{2}}} \sum_{v=-u}^{2N+u} \sin(p'v)\sin(q'v).$$

For diagonal element $p = q$:

$$I(p) = \int_1^N du \frac{\sin^2 p'u}{u^{\frac{3}{2}}} \int_u^{2N-u} dv \sin^2 p'v + \int_{-N}^{-1} du \frac{\sin^2 p'u}{|u|^{\frac{3}{2}}} \int_{-u}^{2N+u} dv \sin^2 p'v.$$

Integration over v gives [12]

$$I(p) = 2N \int_1^N du \frac{\sin^2 p'u}{u^{\frac{3}{2}}} - 2\int_1^N du \frac{\sin^2 p'u}{u^{\frac{1}{2}}} + \frac{1}{2p'}\int_1^N du \frac{\sin 2p'u}{u^{\frac{3}{2}}} - \frac{1}{4p'}\int_1^N du \frac{\sin 4p'u}{u^{\frac{3}{2}}}. \tag{5}$$

We are interested in the modes for which $p' \to 0$. For the trigonometric series the following identity [16] is used:

$$\sum_{n=1}^{\infty} \frac{\sin nx}{n^{\beta}} \cong x^{\beta-1}\Gamma(1-\beta)\cos\frac{1}{2}\pi\beta \ , \text{ for } x \to 0^+, 0 < \beta < 2.$$

So,

$$\frac{1}{2p'}\sum_1^N du \frac{\sin 2p'u}{u^{\frac{3}{2}}} \cong \frac{1}{2p'}(2p')^{\frac{1}{2}}\Gamma(-\frac{1}{2})\cos\frac{3\pi}{4} = \frac{1}{\sqrt{2}}\frac{\sqrt{N}}{\sqrt{p}} \tag{6}$$

$$\frac{1}{4p'}\sum_1^N du \frac{\sin 4p'u}{u^{\frac{3}{2}}} = \frac{\sqrt{N}}{\sqrt{p}} \tag{7}$$

$$2N\sum_{u=1}^{\infty} \frac{\sin^2 p'u}{u^{\frac{3}{2}}} \cong 2N \sum_{u=1}^{\frac{1}{p'}} \frac{(p'u)^2}{u^{\frac{3}{2}}} \approx \frac{4\sqrt{\pi}}{3\sqrt{2}}\sqrt{N}\sqrt{p} \tag{8}$$

$$2\sum_{u=1}^{N}\frac{\sin^2 p'u}{u^{\frac{1}{2}}} = \sum_{u=1}^{N}\frac{1-\cos 2p'u}{u^{\frac{1}{2}}}$$
$$= \sum_{u=1}^{N}\frac{1}{u^{\frac{1}{2}}} - \sum_{u=1}^{N}\frac{\cos 2p'u}{u^{\frac{1}{2}}}$$
$$\cong 2(\sqrt{N}-1) - \frac{1}{\sqrt{2}}\frac{\sqrt{N}}{\sqrt{p}} \tag{9}$$

Using (6),(7),(8) and (9) in (5), $I(p)$ is given by

$$I(p) = \sqrt{N}\left[1.67\sqrt{p} + 1.12\frac{1}{\sqrt{p}} - 2\right],$$

which leads to the following result for ζ_p:

$$\zeta_p = 0.42\,(mk_BT)^{\frac{1}{2}}\left(\frac{R^2}{b^3}\right)\left[\frac{(1.67\sqrt{p} + 1.12\frac{1}{\sqrt{p}} - 2)}{\sqrt{N}}\right] \tag{10}$$

This derivation is true for $p' \to 0$. For a finite chain the $\frac{1}{\sqrt{p}}$ term can not be neglected compared to $\sqrt{p}$. For very large chain, $p' \to 0$ for large p. Thus, $\frac{1}{\sqrt{p}} \ll \sqrt{p}$. In that case, ζ_p would be similar to de Gennes term [5], which is proportional to $\frac{\sqrt{p}}{\sqrt{N}}$. Also from an experimental point of view, only very small p's are important, because relaxation times for large p are very fast and hardly measured experimentally.

Consideration of non diagonal term shows that correlation for different normal modes do not vanish [12]. We leave for future work how this non-diagonal elements in correlation matrix affect the dynamic structure factor.

3 Internal friction in solution

When a polymer is in solution, this mechanism for internal friction is still applicable. In the equation of motion, a random force term must be included to account for the collisions with other monomers. When two monomers collide in vacuum, the non colliding monomers do not know about the event unless they are nearest or next nearest neighbors. But in solution when two monomers will collide, the information of the collision is carried to other monomers by hydrodynamic interactions. We need to know what velocity field would be created for a pair of equal and opposite forces, as determined by the behavior of the Oseen tensor. Velocity field at monomer n due to random force at m is

$$\mathbf{v}_n = \sum \mathbf{H}_{nm} \cdot \mathbf{f}_m,$$

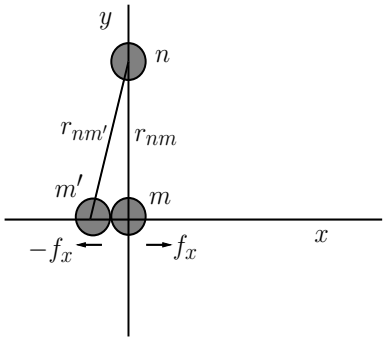

Figure 2: Velocity field created by a pair of random forces. Monomer m is at the origin. Monomer m' is making a head-on collision with monomer m. Monomer n is at a distance r_{nm} from m. The Oseen tensor gives the velocity field at position $\mathbf{r}_{nm}$.

where $\mathbf{H}_{nm}$ is the Oseen tensor:

$$\mathbf{H}_{nm} = \frac{1}{8\pi\eta r_{nm}} \left(\mathbf{I} + \hat{r}_{nm}\hat{r}_{nm}\right).$$

For a pair of force f_x and -f_x, as shown in figure (2), velocity components are [17]

$$v_x = \frac{f_x}{8\pi\eta}\left[\left(\frac{1}{r_{nm}} + \frac{x_{nm}^2}{r_{nm}^3}\right) - \left(\frac{1}{r_{nm'}} + \frac{x_{nm'}^2}{r_{nm'}^3}\right)\right],$$

$$v_{y/z} = \frac{f_x}{8\pi\eta}\left[\frac{x_{nm}\left(y_{nm}/z_{nm}\right)}{r_{nm}^3} - \frac{x_{nm'}\left(y_{nm'}/z_{nm'}\right)}{r_{nm'}^3}\right].$$

From these equations it can be shown that [12] for a pair of forces, $v_n \propto \frac{R^2}{r_{nm}^2} + 0(\frac{1}{r_{nm}^3})$. Since for a Gaussian chain $r_{nm}^2 \propto |n-m|$, the velocity field at monomer n for a pair of equal and opposite forces at monomer m is $\propto \frac{1}{|n-m|}$.

The solution of Zimm model, which includes the hydrodynamic interaction, uses the following Oseen tensor for a Gaussian chain [13]:

$$\mathbf{H}_{nm} = \frac{\mathbf{I}}{6\pi^3|n-m|^{\frac{1}{2}}\eta b} = h(n-m)\mathbf{I}.$$

In terms of normal modes the equation of motion in Zimm model is [13]

$$\frac{\partial \mathbf{X}_p}{\partial t} = \sum h_{pq}(-k_q X_q + f_q),$$

where

$$h_{pq} = \sum_{\infty}^{\infty} h(m)\cos\left(\frac{p\pi m}{N}\right).$$

As in Zimm model if we take $h(m) = m^{-\frac{1}{2}}$, then

$$\sum \frac{\cos(\frac{p\pi m}{N})}{m^{\frac{1}{2}}} \propto \left(\frac{N}{p}\right)^{\frac{1}{2}}.$$

Consider the pair of forces, $h(m) = m^{-1}$, which gives [16]

$$\sum \frac{\cos(\frac{p\pi m}{N})}{m} = -\ln\left(2\sin\left(\frac{p\pi}{2N}\right)\right). \tag{11}$$

Since the right side of equation (11) is negligible compared to $(\frac{N}{p})^{\frac{1}{2}}$, the hydrodynamic interaction due to a pair of equal and opposite forces is negligible compared to the hydrodynamic interaction from a single random force. Therefore, we can safely say that the momentum transfer from monomer to monomer is direct and does not involve solvent. Thus, the mechanism of internal friction in vacuum is applicable in solutions as well.

4 Conclusion

We have shown first-principles calculations of internal friction. For polymers in vacuum, the dynamics of a single chain can be described by the Langevin equation where the random forces are correlated. For polymers in solution, the Langevin equation contains two random force terms. One arising from the solvent particles and the other from collisions with other monomers, and these two are utterly uncorrelated. We have shown that hydrodynamic interaction term for random forces caused by collisions between monomers is negligible compared to the term that arises due to solvent particles. Therefore, the dynamics in solution can be described by the Zimm model with an extra friction term which is internal; extrapolation of solvent viscosities to zero would reveal this residual dissipation.

Acknowledgements. The author wish to thank Prof. Sergei Obukhov who provided valuable advice and comments to the undertaking of the research summarised here.

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Received: November 30, 2014; Published: January 9, 2015