Polymer brush bilayers under stationary shear motion at linear response regime: A theoretical approach

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ABSTRACT:

Statistical mechanics is employed to tackle the problem of polymer brush bilayers under stationary shear motion. The article addresses, solely, the linear response regime in which the polymer brush bilayers behave very much similar to the Newtonian fluids. My approach to this long-standing problem split drastically from the work already published *Kreer, T*, Soft Matter, 12, 3479 (2016). It has been thought for many decades that the interpenetration between the brushes is source of the friction between the brush covered surfaces sliding over each other. Whiles, the present article strongly rejects the idea of interpenetration length in that issue. Instead, here, I show that structure of the whole system is significant in friction between brush covered surfaces and the interpenetration is absolutely insignificant. The results of this research would blow one's mind about how the polymer brush bilayers respond at small shear rates.

Keywords: Polymer brush bilayers, Stationary shear motion, Linear response regime, Newtonian fluids

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INTRODUCTION

Polymers are linear macromolecular structures that are composed of repeating building blocks of atomic or molecular size i.e. monomers. Typically, polymers bear 10^4 to 10^5 monomers per chain (degree of polymerization) in biological systems[1]. In principle, the word polymer is devoted to long linear macromolecules with many monomers. The connectivity between monomers in chain is established through the Covalent bond in which monomers share their valence electron together. In 1827, R. Brown discovered that particles at molecular and atomic scale undergo thermal fluctuations. Since, monomers undergo thermal agitation as well, therefore the whole polymer chain undergoes all possible conformations in the course of time. However, at thermal equilibrium the chain stays at a certain average length. This length is determined by *entropic elasticity* (which shrinks the chain) from one hand and the *steric repulsion* among monomers (which stretches the chain) on the other hand.

One of the most interesting polymeric structures that exists in many biological systems is the polymer brushes[2]. Polymer brushes are composed of linear chains that are chemically grafted into a surface. The steric repulsion among monomers of nearby chains stretches the chains strongly in the perpendicular direction. The brush like structures could be found as Glycol on the outside of cell membranes as well as aggregan in synovial fluids of mammalian joints. Since the thickness of the brush layer is easily controllable by varying molecular parameters, therefore one could tune the surface properties by brushes. Polymer brush bilayers (PBB) are observed in synivial joints of mammals and they are responsible for reduction of friction between the bones sliding over each other. Moreover, it has been also known that the PBBs are responsible for suppression of the mechanical instabilities in synovial joints. To investigate such a situation, one would normally take two parallel surfaces with a certain distance and each surface covered by a brush that are similar in molecular parameters. The brushes got to be at intermediately compressed state to make balance between compression and interpenetration. The most simplified motion that resembles the synovial joints motion in walking, could be the shear motion where surfaces move in opposite directions with the same velocity. Depending on the shear rates, the PBBs response to the

shear forces are divided into two regimes. The regime of small shear rates or the linear response regime and the regime of large shear rates. In this article, I focus on the linear response regime where the PBBs behave like the Newtonian fluids. Note that, here I do not address the regime of large shear rates where shear thinning effects appear. It has been taught, for few decades, that the interpenetration between the brushes is significant in producing friction between sliding surfaces[4]. Here, I provide theoretical considerations that strongly rejects the significance of interpenetration length in the friction. Instead, my theory suggests that the structure of whole system is significant in friction.

In the next section, I describe my theory in detail and make comparisons with the existing theoretical approaches to the same problem.

THEORETICAL DESCRIPTION

Newtonian fluids

Let us consider a Newtonian fluid which is restricted between two flat plates of surface area A and distance D. Under the shear motion the flat plates move in opposite directions with velocity v. In such situations, the governing equations would be the Stokes equations as follows,

$$\eta\, \boldsymbol{\nabla}^2 \boldsymbol{u}(\boldsymbol{x}, t) \;=\; \boldsymbol{\nabla} p \tag{1}$$

where η is the fluid viscosity, $\boldsymbol{u}(\boldsymbol{x}, t)$ the fluid velocity and p the fluid pressure. Assume that the flat plates are in xy plane such that the bottom plate is located at $z = 0$ and the top plate at $z = D$. If the shear direction is supposed to be in the x direction, then the following differential equation holds,

$$\eta\, \frac{\partial^2 u_x}{\partial z^2} \;=\; \frac{\partial p}{\partial x} \tag{2}$$

In the absence of external flow, one would set $\frac{\partial p}{\partial x} = 0$. By considering the no-slip boundary conditions i.e. $u_x(z = 0) = -v$ and $u_x(z = D) = v$, the solution of Eq. (2) would be,

$$u_x(z) = \dot{\gamma}\, z - v \tag{3}$$

Where $\dot{\gamma} = 2v/D$ is the shear rate. Therefore, the velocity profile is linear in z and vanishes at the center of channel. The stress tensor is given as follows,

$$\mathbf{\Pi} = \eta\, \boldsymbol{\nabla u} - p\boldsymbol{I} \tag{4}$$

Which implies the following results for normal and shear stresses,

$$\mathbf{\Pi}_n = p \qquad\qquad \mathbf{\Pi}_s = \eta\, \dot{\gamma} \tag{5}$$

It turns out that the viscosity and the equation of state of the fluid give a full description of the response under stationary shear motion. That is an important property of the Newtonian fluids. Having reviewed the Newtonian fluids under stationary shear, I will consider PBBs under stationary shear in the following.

PBBs under stationary shear

Now let us consider brushes that are grafted onto the flat plates and are suspended in a solvent. The equation of state of a PBB has been already calculated[6] and it is given as follows,

$$\begin{aligned} p &= \frac{1}{240\, a^4\, b\, N^4\, D^4}(435\, D^8 + 720\, a^2\, b\, D^5\, N^3\sigma - 187\, D^7\, \chi_0^{1/3} - 192\, a^2\, b\, D\, N^3\sigma\chi_1\chi_0^{1/3} \\ &+ 187\, D^6\, \chi_0^{2/3} - 600\, a^2\, b\, N^3\, \sigma\, \chi_1\, \chi_0^{2/3} + 2\, D^4\, \chi_0^{1/3}\, \chi_2 + 4\, D^3\, \chi_0^{2/3}\, \chi_3) \end{aligned} \tag{6}$$

where a is the Kuhn length or monomer size, b the second Virial coefficient, N the degree of polymerization, σ the grafting density and I have introduced the following volumes for the sake of having shorter formula,

$$\chi_0 = (6\, a^2\, b\, N^3\, \sigma - D^3 + 2\sqrt{3\, a^2\, b\, N^3\, \sigma\, (3\, a^2\, b\, N^3\, \sigma - D^3)}) \tag{7}$$

$$\chi_1 = (3\, a^2\, b\, N^3\, \sigma + \sqrt{3\, a^2\, b\, N^3\, \sigma\, (3\, a^2\, b\, N^3\, \sigma - D^3)}) \tag{8}$$

$$\chi_2 = (-351\, a^2\, b\, N^3\, \sigma + 151\, \sqrt{3\, a^2\, b\, N^3\, \sigma\, (3\, a^2\, b\, N^3\, \sigma - D^3)}) \tag{9}$$

$$\chi_3 = (-558\, a^2\, b\, N^3\, \sigma + 169\, \sqrt{3\, a^2\, b\, N^3\, \sigma\, (3\, a^2\, b\, N^3\, \sigma - D^3)}) \tag{10}$$

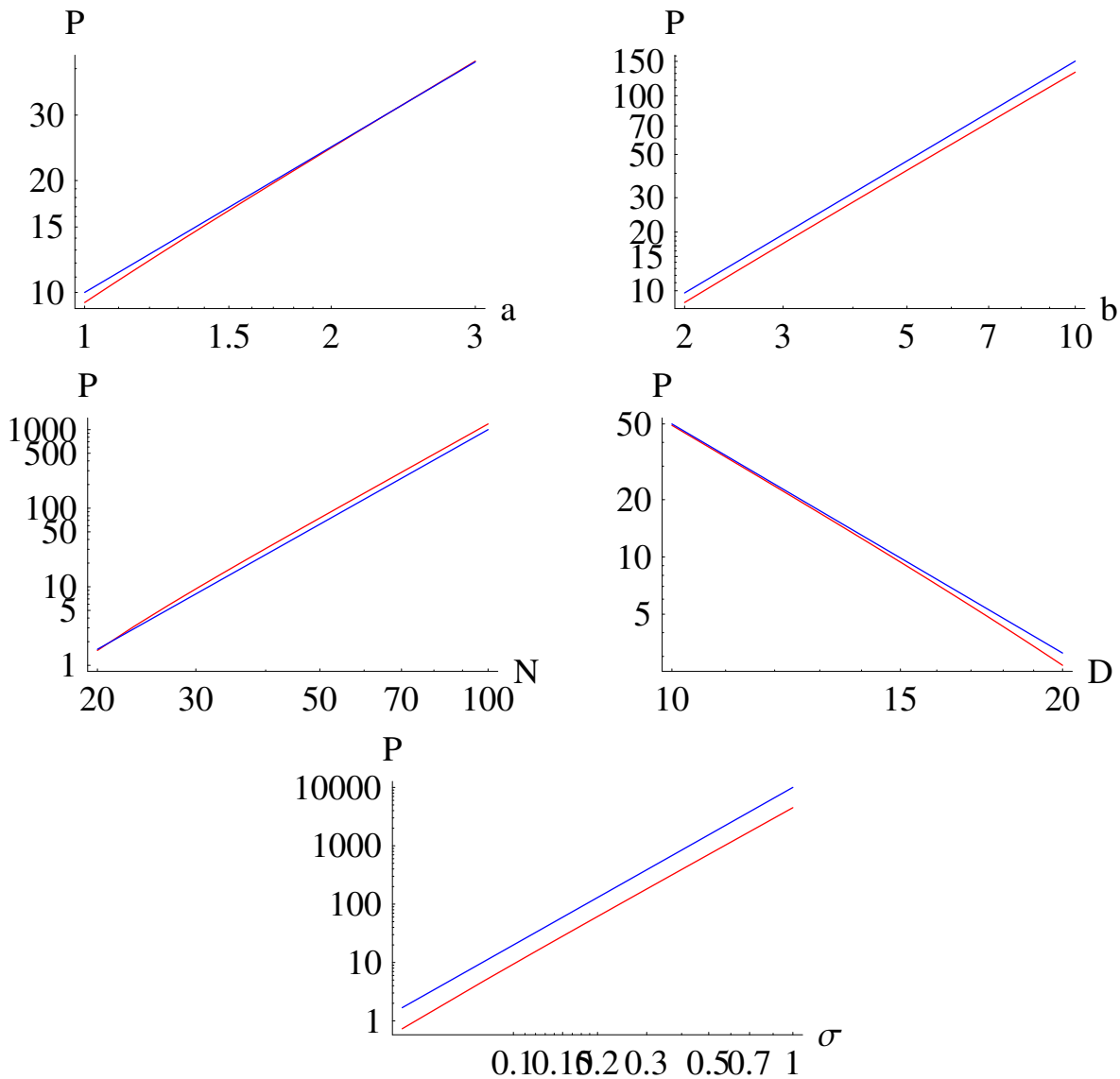

Figure 1: The equation of state of the PBBs in terms of system parameters. The plots indicate universal power laws as $p \sim a^{1.3}\, b^{1.7}\, \sigma^{2.7}\, \left(\frac{N}{D}\right)^4$.

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Fig. 1 shows that the pressure follows the universal power laws as given below,

$$p \sim a^{1.3}\, b^{1.7}\, \sigma^{2.7} \left(\frac{N}{D}\right)^{4} \tag{11}$$

The shear forces do not change the equation of state as long as the linear response regime holds. The linear response regime is valid if the Weissenberg number W is smaller than unity. The Weissenberg number is a dimensionless number that is defined as follows,

$$W = \dot{\gamma}\, \tau_c \tag{12}$$

where $\tau_c = \frac{N^2 a^2 \xi}{3\pi^2\, k_{\mathrm{B}} T}$ is the critical time scale below which the chains can relax and ξ the monomer friction constant. In principle, τ_c is the largest mode of the Rouse time scale which is taken into account as the largest relaxation time of polymer chains at melt concentration without hydrodynamic interactions between monomers[5]. Therefore, all of my calculations are valid for ($W \ll 1$) that the shear forces are not able to overcome the entropic forces that make monomers diffuse.

So far, I have given a full description of the PBB equation of state as well as the validity range of the linear response regime. According to Eq. (5), we know the normal stress as $\mathbf{\Pi}_n = p$. To calculate the shear stress for the PBBs, one has to get to know about the viscosity of the PBBs. Actually, viscosity is an intrinsic property of any substance. According to the statistical mechanics, the viscosity of any system is equal to its equation of state multiplied by the average time between two successive collisions between its particles i.e *collision time*[3]. For PBBs, the collision time of monomers can be calculated as follows. The Rouse time scale tells us how much time it takes for a monomer to travel a certain distance by diffusion. Therefore, one could assume that for the PBBs, the mean free path or the average distance between monomers is $(2N\sigma/D)^{-1/3}$ and the diffusion constant of monomers is $(k_{\mathrm{B}}\, T/N\xi)$. By dividing the mean free path squared by the diffusion constant, one would get the following time scale as the collision time for monomers in a PBB,

$$\tau = \left(\frac{2\sigma}{D}\right)^{-2/3} \frac{N^{1/3}\xi}{k_{\mathrm{B}} T} \tag{13}$$

This is the shortest time scale during which monomers are kicked by other monomers. Note here that, this is from the kicks that monomers get from the solvent molecules because here I assume that monomers are much larger than solvent molecules. Having calculated the collision time, one would calculate the PBB viscosity as $\eta = p\,\tau$. Eq. (14) shows that the PBBs viscosity follows the universal power laws as given bellow,

$$\eta \sim \frac{a^{1.3} b^{1.7} \sigma^{2.03} \xi}{2^{2/3} k_{\mathrm{B}} T D^{5/2}} N^{13/3} \tag{14}$$

The viscosity increases strongly by N and it strongly decreases by D. Now that the viscosity as well as the equation of state are calculated, one would calculate the shear stress and the kinetic friction coefficient as following,

$$\mathbf{\Pi}_s \sim \frac{a^{1.3} b^{1.7} \sigma^{2.03} \xi}{2^{2/3} k_{\mathrm{B}} T D^{5/2}} N^{13/3} \dot{\gamma} \tag{15}$$

$$\mu = \tau\,\dot{\gamma} = \left(\frac{2\sigma}{D}\right)^{-2/3} \frac{N^{1/3} \xi}{k_{\mathrm{B}} T}\,\dot{\gamma} \tag{16}$$

Note here that, in the friction coefficient equation, the shear rate itself is a function of the D. It means that the actual dependence upon the plates distance is $D^{-1/3}$. In the next section, I proceed to make conclusions and discuss the final arguments. Also, I would like to discuss some advantages of my approach to the problem of the PBBs under stationary shear.

CONCLUDING REMARKS

In this article, I addressed the polymer brush bilayers under stationary shear motion at linear response regime. At linear response regime the shear forces are weaker than the entropic forces and are not able to change the equation of states. However, the normal and shear stresses split by presence of the weak shear forces. This is the linear response regime in which the PBBs behave some what similar to Newtonian fluids. The only thing the PBBs have common with the Newtonian fluids is the linear dependence of transport quantities upon the shear rate. Clearly, the dependence upon molecular parameters are totally different from those of the Newtonian fluids.

The idea here is that the whole structure of the PBB system is significant to produce friction under shear. The complex processes at molecular scale such as collision time and the equation of state are apparently responsible for the friction and definitely the interpenetration[4] is not responsible for that. I reject the significance of the interpenetration between the brushes in friction and one possible answer could be given as following. This is accepted that every shear induced force will be relaxed in the system as long as the linear response regime holds. Now, in this condition, how to admit that the stress produced in the narrow interpenetration region will be transferred to the plates without being relaxed. Another argument for rejecting the significance of the interpenetration would be laying in the nonlinear response regime of the PBBs. It has been observed that at Weissenberg numbers larger than unity, the shear stress follows sublinear regime while the interpenetration length vanishes. However, the shear stress still is non-zero. So it would seem irrational to relate those two effects to each other. Remarkably, the present approach indicates that the PBB viscosity decreases by the plates distance which is again well anticipated. When the plates get more distant, then at a certain distance the entropic effects disappear. This can happen by decrease of the monomer concentration as well as increase of the collision time. It is shown that the viscosity increases by molecular parameters such as the degree of polymerization, the second Virial coefficient, the grafting density and the monomer friction constant. The strong dependence of the viscosity upon the polymerization index tells us that the connectivity of monomers in the backbone of chains is very significant rather than the number of chains i.e. the grafting density.

The kinetic friction coefficient decreases by the plates distance as well as grafting density and it increases by the other molecular parameters. These are rational results based on the fact that more distant plates make smaller concentration and larger grafting densities give rise to more stretched chains, and therefore, more ordered system. The order is a source of the lower viscosity.

The problem of PBBs under stationary shear at nonlinear response regime would be the next step of my research. Moreover, the non-equilibrium conditions like shear inversions or Polyelectrolyte brush bilayers could be candidates for the future studies.

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