

# Effective thickness of adsorbed polymer in a shear field

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The effective thickness of the adsorbed polymer layer in a linear shear field was investigated theoretically. It is found that, when the shear strength is weaker than a certain critical value, distribution of segments perpendicular to the field is unaltered from that at equilibrium, but when the shear strength goes over the critical value, the distribution changes abruptly according to the nature of the adsorption.

(Keywords: adsorbed polymer; effective thickness; shear field; change of thickness; non-linear stretching; loop-train-tail)

## INTRODUCTION

Polymer adsorption is related to many practical and academic problems. One fundamental interest is concerned with the conformational properties of the flexible chains adsorbed onto a flat surface, and many theoretical and experimental investigations have been made in this respect. Although many theoretical papers have investigated the equilibrium case, the experimental information can only be obtained by indirect measurements for ellipsometry, hydrodynamical and spectroscopic treatments etc. In particular, hydrodynamical studies are always related to the non-equilibrium conformational behaviour of adsorbed polymers, in spite of the great importance of the investigation of polymer adsorption.

DiMarzio and Rubin<sup>1</sup> have solved the problem of a chain of beads which is attached to a surface via a Hookean spring and suffers a linear shear field of a viscous fluid with no hydrodynamic interaction. Fortunately, they found that the distribution of the beads along the direction normal to the surface is not influenced by the linear shear field. This situation will not be altered as long as the chain deforms linearly due to external forces even when the effect of the excluded volume of the chain is taken into account. In fact, it is well known that the deformation is linear when the external force is weak. Thus, in a weak linear shear flow, where the hydrodynamic interactions are also small and negligible, the arguments of the conformational properties based on the equilibrium distribution (in the normal direction to the surface) can be applied to the non-equilibrium system.

On the contrary, when the shear flow becomes much stronger, the situation must be altered drastically as shown by a recent experimental study by Gramain and Myard<sup>2</sup>. They show that the hydrodynamic thickness of the adsorbed polymers increases abruptly when the average velocity of the solvent exceeds a certain value.

Here, we will attempt to explain the sudden increase of the effective hydrodynamic thickness of the adsorbed

polymers due to the strong shear flow by considering the conformational properties in the velocity field of the solvent.

## PHENOMENOLOGY

de Gennes<sup>3</sup>, and Varauqui and Dejardin<sup>4</sup> have investigated, for the capillary flows, the problem of the effective hydrodynamic thickness where the concentration of the adsorbed polymer segments decreases exponentially with increasing distance from the surface. Here, we will reconsider this problem for the case of a linear shear flow along a flat surface.

The velocity,  $\vec{v}$ , of the incompressible solvent in the solution containing frictional polymer molecules can be determined by Debye-Bueche's theory from the following equation

$$-\eta \nabla^2 \vec{v} + \vec{\nabla} p + n \zeta \vec{v} = 0 \quad (1)$$
$$\vec{\nabla} \cdot \vec{v} = 0$$

where  $n(\vec{r})$ ,  $\eta$  and  $p$  are the segment density, viscosity of the solvent and the pressure respectively, and  $\zeta$  denotes the coefficient of friction between a segment and the solvent. We have neglected the fluctuational motions of the segments. We will set the  $x$ -axis in the direction of the solvent flow, and take the  $y$ -axis as normal to the surface. Thus the flow field  $\vec{v}(\vec{r})$  is given by

$$\vec{v}(\vec{r}) = (v(y), 0, 0) \quad (2)$$

We will assume that the solvent flow far from the surface is a simple Couette flow given by  $v(y) = ey + \text{constant}$ ,  $e$  being the external shear rate, and that the pressure is gradient free;  $\vec{\nabla} p = 0$ .

In order to see the relation between the effective hydrodynamic thickness and the distribution of the polymer segments adsorbed on the flat surface, we will assume a simple distribution:

$$n(\vec{r}) = n(y) = \begin{cases} \text{constant} \equiv v & \text{for } y < y_0 \\ 0 & \text{for } y > y_0 \end{cases} \quad (3)$$

Then, equation (1) is reduced to

$$\left. \begin{aligned} \eta \frac{d^2 v_{<}}{dy^2} &= v \zeta v_{<} & \text{for } y < y_0 \\ \eta \frac{d^2 v_{>}}{dy^2} &= 0 & \text{for } y > y_0 \end{aligned} \right\} \quad (4)$$

These equations can be easily solved upon the boundary conditions

$$\begin{aligned} v_{<}(y_0) &= v_{>}(y_0) \\ v_{<}(0) &= 0 \\ \left. \frac{dv_{<}}{dy} \right|_{y_0} &= \left. \frac{dv_{>}}{dy} \right|_{y_0} = e \end{aligned} \quad (5)$$

The third condition is assumed in order to express the continuous mean distribution of flexible polymer segments swaying in the flow penetrating them. Thus, we have

$$v_{<}(y) = \frac{e}{\kappa} \frac{e^{\kappa y} - e^{-\kappa y}}{e^{\kappa y_0} + e^{-\kappa y_0}} \quad \text{for } y < y_0 \quad (6a)$$

$$v_{>}(y) = e(y - y_0) + \frac{e}{\kappa} \tanh \kappa y_0 \quad \text{for } y > y_0 \quad (6b)$$

where  $\kappa^{-1} = \sqrt{\eta/v\zeta}$  is a length which can be used as a measure of the 'penetration' rate of the flow. Now, we define the effective thickness  $\lambda$  as

$$v_{>}(\lambda) = 0$$

Then, this  $\lambda$  is given by

$$\lambda = y_0 - \frac{1}{\kappa} \tanh \kappa y_0 \quad (7)$$

When the adsorbed polymers are dilute, we can take  $\kappa y_0 \ll 1$  and equation (7) tends to

$$\lambda \sim (\kappa^2 y_0^2) y_0 \quad (8)$$

It should be noted that this effective thickness  $\lambda$  is not sensitive to the segments near the surface  $y \ll \lambda$  because the absolute value of the solvent velocity is very small there. Important factors affecting  $\lambda$  are the effective width  $y_0$  of the normal distribution of the adsorbed polymers and the effective density  $v$  of the active segments.

Hereafter, we will assume that the adsorbed polymers are dilute ( $\kappa y_0 \ll 1$ ) but that the thickness  $\lambda$  is sufficiently larger than that of the monolayer.

## CONFORMATIONAL BEHAVIOUR

In this section, we will concentrate on the problem of the conformational distribution of the adsorbed polymers under the influence of a linear shear field due to solvent flow. For this we use some assumptions which are inconsistent with the situation discussed in the previous section. For example, we will assume in this section a linear shear field of the form:

$$\vec{v}(\vec{r}) = (v_e(y), 0, 0) = (ey, 0, 0) \quad (9)$$

instead of equations (6a) and (6b). It may, however, be expected that their effects on our results will be negligibly small provided the adsorbed polymers are dilute.

When the applied shear field is weak, the distortion of the adsorbed polymers is small and should be proportional to the shear force  $F$ . DiMarzio and Rubin have solved this problem by the beads and spring model<sup>1</sup>. It is well known, however, that when the shear field becomes stronger, the polymers distort non-linearly and their theory therefore becomes inapplicable.

For a dilute solution of flexible polymers under ultra-high velocity gradients, de Gennes has investigated its coil-stretch transition<sup>5</sup>. This behaviour must be the same as that the adsorbed system except that the distribution of polymers is limited to the region  $y > 0$  and, in our problem the external forces are balanced with the adsorption forces.

As to the elastic properties, Webman, Lebowitz and Kalos have recently made a computer simulation on a model polymer chain having excluded-volume interactions<sup>6</sup>. According to their results the stretching of an isolated polymer chain is linear in the case of weak and moderate external forces. But, after passing a rather narrow cross-over region (Oono, Ohta and Freed give a broad cross-over region by theoretical argument<sup>7</sup>), it becomes non-linear in the sense that the reponse is proportional to the 2/3 power of the applied force.

In the present calculation, however, we will adopt the following phenomenological form of the restoring force to a polymer chain<sup>5</sup>:

$$\vec{F} = -kE(r)\vec{r}, \quad k = 3k_B T/R_0^2 \quad (10)$$

where  $\vec{r}$  stands for the position measured from a certain central point of the adsorption on the surface,  $k$  corresponds to the spring constant in the 'dumbell' model ( $R_0$  is a certain equilibrium distance of the chain without external forces), and  $E(r)$  is a reponse factor. The function  $E(r)$  is unity at small  $r$  but tends to increase for  $r > r_c$  and diverges for  $r \rightarrow Na$  ( $N$  is the number of segments of the chain and  $a$  is the length of the unit link) as shown in Figure 1.

Now, we will define the distribution function  $\Phi_e(\vec{r})$  of the polymer segments in a stationary state under the shear field  $\vec{v}(\vec{r})$  of equation (9). Here, the inferior letter  $e$  denotes the external shear rate, and sometimes we replace  $e$  with 0 for the quantity free from the external forces. We will put no restriction on the form of this  $\Phi_e(\vec{r})$  such as  $n(y)$  in the previous section. It is subjected only to the following boundary conditions;

$$\Phi_e(\infty) = 0, \quad \Phi_e(\vec{r})|_{y=0} \neq 0 \quad (1)$$

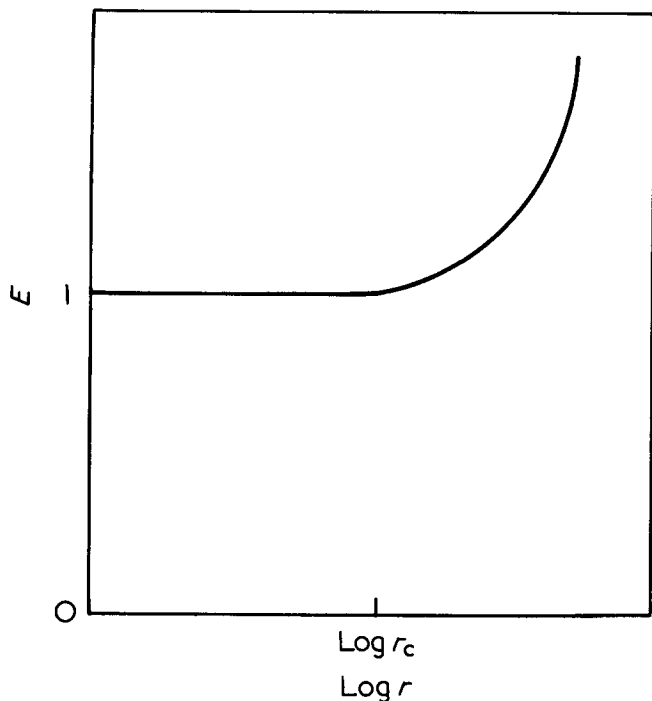
The associated current  $\vec{j}_e \Phi_e(\vec{r})$  can be given as

$$\vec{j}_e \Phi_e(\vec{r}) = \Phi_e \vec{v} + D_e \left\{ \Phi_e \frac{1}{k_B T} \vec{F} - \vec{\nabla} \Phi_e \right\} \quad (12)$$

where  $D_e$  is the diffusion coefficient given by the theory of Brownian motion and depends on  $\vec{v}$ . The behaviour of  $D_e$  has been discussed phenomenologically by de Gennes<sup>5</sup>.

Conservation of the probability and the stationary condition are imposed on this current

$$\vec{\nabla} \cdot \vec{j}_e \Phi_e(\vec{r}) = 0$$



**Figure 1** Schematic diagram of  $E(r)$  vs.  $\log r$ .  $E(r)$  is unity for  $r < r_c$  but tends to increase abruptly for  $r > r_c$ .

that is,

$$\vec{\nabla} \cdot (\Phi_e \vec{v}) + \vec{\nabla} \cdot \left( D_e \left\{ \Phi_e \frac{1}{k_B T} \vec{F} - \vec{\nabla} \Phi_e \right\} \right) = 0 \quad (14)$$

Substituting into relations (9) and (10), we have

$$\vec{\nabla} \cdot (\Phi_e e y \vec{e}_x) - \vec{\nabla} \cdot \left( D_e \left\{ \Phi_e \frac{3}{R_0^2} E(r) \vec{r} + \vec{\nabla} \Phi_e \right\} \right) = 0 \quad (15)$$

where  $\vec{e}_x = (1, 0, 0)$ . Using equation (15), we can derive the moments

$$\langle x^i y^j z^k \rangle_e \equiv \int_{-\infty}^{\infty} dx \int_0^{\infty} dy \int_{-\infty}^{\infty} dz x^i y^j z^k \Phi_e(\vec{r}) \quad (16)$$

where  $i, j$  and  $k$  stand for 0 or arbitrary positive integers.

We are especially interested in the moments preceding the second order and in deriving them, we will prepare some general relations obtained by partial integrations under the boundary conditions of equation (11) as follows

$$\begin{aligned} \int_{-\infty}^{\infty} dx dz \int_0^{\infty} dy y \Phi_e &\equiv \langle y \rangle_e \equiv \chi_e \\ \int_{-\infty}^{\infty} dx dz \int_0^{\infty} dy y \frac{\partial^2 \Phi_e}{\partial y^2} &= - \int_{-\infty}^{\infty} dx dz \Phi_e(r) \Big|_{y=0} \equiv -\varphi_e \quad (17) \\ \int_{-\infty}^{\infty} dx dz x \Phi_e(\vec{r}) \Big|_{y=0} &\equiv \hat{x}_e \quad \text{etc.} \\ \int_{-\infty}^{\infty} dx dz \int_0^{\infty} dy (x^2, y^2, z^2) \nabla^2 \Phi_e &= (-2, -2, -2) \quad \text{etc.} \end{aligned}$$

If we want to determine the conformational distribution concretely and to consider the hydrodynamical interaction explicitly, we need to give both the diffusion coefficient  $D$  and the function  $E$  as functions of  $\vec{r}$ , i.e.,  $D(\vec{r})$  and  $E(\vec{r})$ . Multiplying equation (15) by  $x^i y^j z^k$  where  $i+j+k \leq 2$ , and integrating the overall allowed volume, we obtain

$$\begin{aligned} \langle D(\vec{r}) \rangle_e + e \langle xy \rangle_e + \left\langle x \frac{\partial D(\vec{r})}{\partial x} \right\rangle_e - \langle x^2 D(\vec{r}) E(\vec{r}) \rangle_e &= 0 \\ -e \langle y^2 \rangle_e + \left\langle y \frac{\partial D(\vec{r})}{\partial x} \right\rangle_e + \left\langle x \frac{\partial D(\vec{r})}{\partial y} \right\rangle_e + 2 \langle xy D(\vec{r}) E(\vec{r}) \rangle_e \\ - \langle D(\vec{r}) x \rangle_{e,2} &= 0 \quad (18a) \end{aligned}$$

$$- \langle D(\vec{r}) \rangle_e - \left\langle y \frac{\partial D(\vec{r})}{\partial y} \right\rangle_e + \langle y^2 D(\vec{r}) E(\vec{r}) \rangle_e = 0$$

$$- \langle D(\vec{r}) \rangle_e - \left\langle z \frac{\partial D(\vec{r})}{\partial z} \right\rangle_e + \langle z^2 D(\vec{r}) E(\vec{r}) \rangle_e = 0$$

... etc.

where

$$\langle \dots \rangle_{e,2} \equiv \int_{-\infty}^{\infty} dx dz \dots \Phi_e(r) \Big|_{y=0} \quad (18b)$$

In our qualitative arguments, however, we will treat  $D$  and  $E$  as constants which are determined only by  $e$ , and will denote them by  $D_e$  as previously defined and  $E_e$ , respectively. Then equation (18) can be reduced to

$$\begin{aligned} e \langle y \rangle_e = \chi_e = D_e E_e \langle x \rangle_e \\ \langle z \rangle_e = 0 \\ D_e + e \langle xy \rangle_e - D_e E_e \langle x^2 \rangle_e = 0 \quad (19) \\ e \langle y^2 \rangle_e - D_e E_e \langle xy \rangle_e + D_e \hat{x}_e = 0 \\ 1 - E_e \langle y^2 \rangle_e = 0 \\ 1 - E_e \langle z^2 \rangle_e = 0 \end{aligned}$$

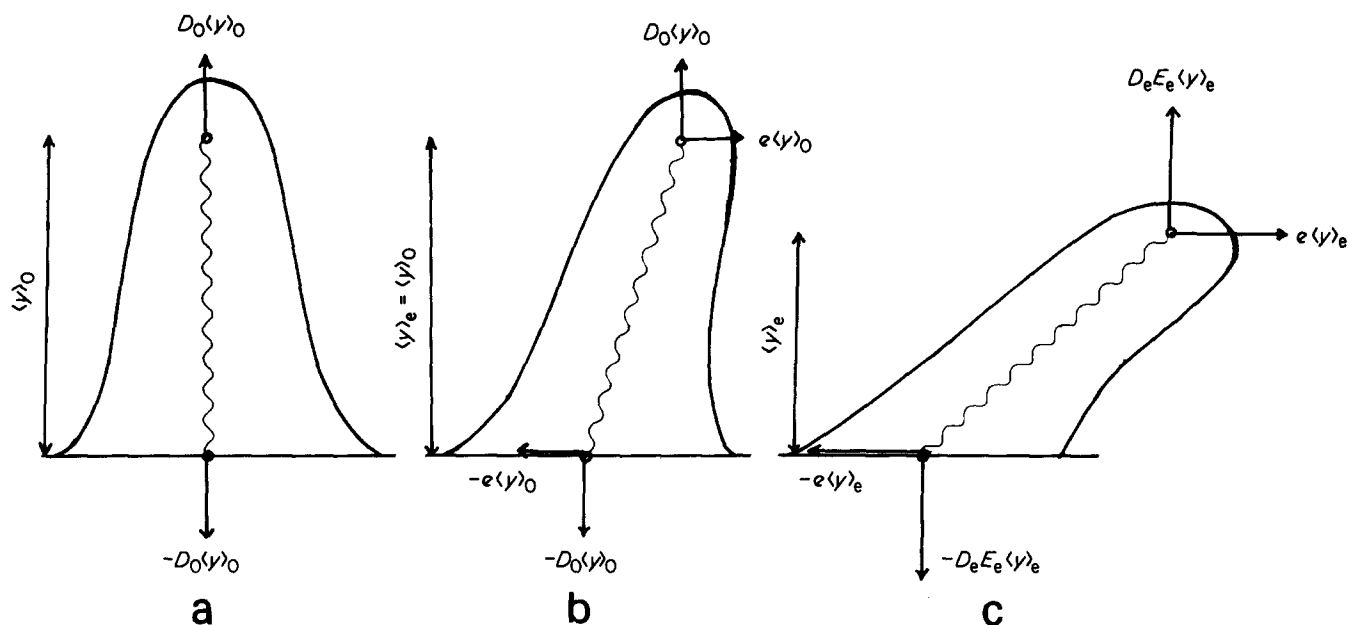
Now, we will consider equation (19) in the following three cases.

(i)  $e=0$ : In this case,  $D_e$  and  $E_e$  are to be expressed as  $D_0$  and 1 respectively, and the state is in equilibrium. The results are

$$\begin{aligned} \langle x \rangle_0 = \langle z \rangle_0 = 0 \\ \langle y \rangle_0 = \chi_e \\ \langle y^2 \rangle_0 = 1 \quad (20) \\ \langle z^2 \rangle_0 = 1 \\ \langle xy \rangle_0 = \hat{x}_0 \end{aligned}$$

Notice here that the segments are attracted in the  $y$ -direction by the adhesion from the anchored segments and balance with them, as shown by Figure 2a.

(ii)  $0 < e < e_c$ : The values of  $D_e$  and  $E_e$  stay near to  $D_0$  and unity respectively. The state is stationary but not in equilibrium. The results obtained by DiMarzio and Rubin are as follows<sup>1</sup>



**Figure 2** Schematic diagram of  $\Phi_e$ . (a) The case of (i) ( $e=0$ ): in equilibrium state. Expansion force of the chain is balanced by the adhesion force. (b) The case of (ii) ( $e < e_c$ ): Chain is balanced by sliding parallel to  $x$ -axis because of the shear force, but the height of the chain does not change. (c) The case of (iii) ( $e > e_c$ ): Expansion force becomes much stronger than for cases (i) and (ii). If the adhesion force is strong enough to support the adsorption of the chain, the height of the chain becomes abruptly small

$$\begin{aligned}
 e\langle y \rangle_e &= D_0 \langle x \rangle_e \\
 \langle x^2 \rangle_e - \frac{e}{D_0} \langle xy \rangle_e - 1 &= 0 \\
 \langle xy \rangle_e - \hat{x}_e - \frac{e}{D_0} \langle y^2 \rangle_e &= 0 \\
 \langle y^2 \rangle_e &= 1 \\
 \langle z^2 \rangle_e &= 1
 \end{aligned} \quad (21)$$

and hence

$$\langle x^2 \rangle_e = 1 + \frac{e^2}{D_0^2} + \frac{e\hat{x}_e}{D_0} \quad (22)$$

As can be seen above, the distribution along the  $y$ -axis is not disturbed by  $v$ . Hence the balance of forces in the  $y$ -direction is the same as the case (i). This case corresponds to Figure 2b.

(iii)  $e > e_c$ : Polymers begin to stretch non-linearly, i.e.  $E_e > 1$ . The diffusion coefficient  $D_e$  will then start to deviate from  $D_0$ . It decreases with increasing  $e$  as proposed by de Gennes<sup>5</sup>. In order to maintain the stationary state, the following relations have to be satisfied:

$$\begin{aligned}
 e\langle y \rangle_e &= D_e E_e \langle x \rangle_e \\
 D_e + e\langle xy \rangle_e - D_e E_e \langle x^2 \rangle_e &= 0 \\
 e\langle y^2 \rangle_e - D_e E_e \langle xy \rangle_e - D_e \hat{x}_e &= 0 \\
 1 - E_e \langle y^2 \rangle_e &= 0 \\
 1 - E_e \langle z^2 \rangle_e &= 0
 \end{aligned} \quad (23)$$

and hence

$$\langle y^2 \rangle_e = 1/E_e \quad (24)$$

The distribution along the  $y$ -axis is depressed to  $1/\sqrt{E_e}$ , and a new balance of forces is required in order to maintain this distribution. This means that the adhesion force in the  $y$ -direction must increase  $\sqrt{E_e}$  times more

than that in the weak field case. This case is shown schematically in Figure 2c.

Consequently, when the adhesion force is strong enough to maintain this new balance of forces, the conformational distribution of segments changes smoothly to the new state, but, when the adhesion force is not sufficiently strong, the distribution changes abruptly.

## DISCUSSION

Earlier we found that, in the external shear field of the solvent flow, the effective thickness of the adsorbed polymers can be given approximately by the effective width  $y_0$  and that the mean density,  $v$ , of the segments does not depend on the strength of the shear field directly. In the previous section an analysis of the effect of the shear field on the conformational distribution was made. It was found that  $\langle y^2 \rangle$ , corresponding to the square of the effective width  $y_0$ , does not change for  $e$  values smaller than  $e_c$ , but that it does contract to  $y_0/\sqrt{E_e}$  ( $E_e > 1$ ) when  $e$  is greater than  $e_c$ . This contraction of the distribution is caused by the stretching due to the strong shear field and can be maintained by an increase in the adhesion from the segments attached to the surface.

In order to understand the features of our problem qualitatively we will now make some rough deductions. Although we need to analyse the detailed behaviour of the effective thickness, we will ignore the effects caused by the decrease in  $D_e$ . We may then consider the following three cases; (a) Only one end of the polymer chain is tightly bound to the surface and there are no trains. (b) The polymer has trains tightly anchored to the surface. (c) There are two kinds of trains: one is tightly anchored to the surface (including the tightly attached end) and the other is 'floating' near the surface. The last case could often occur because of the roughness of the surface.

For cases (a) and (b), the effective thickness,  $\lambda$ , will contract suddenly to  $\sim (1/\sqrt{E_e})\lambda_0$  when  $e$  becomes

greater than  $e_c$ , because  $y$  thins down even though  $y_0 n$  remains unchanged. On the contrary, in the case (c), we can predict abrupt increases in the effective thickness. If some loops and/or tails are anchored by the floating trains (whose adhesive forces might be weak), then the trains, which are stable when  $e$  is smaller than  $e_c$ , begin to leave the surface when  $e$  becomes greater than  $e_c$ . The non-linear restoring forces then overcome the normal adhesion to the surface. This leads to stretching of the loops and/or trains and some of them start to become untied. This, of course, results in an increase in the effective thickness because of the elongation of the arms of loops and/or tails. Such a situation may occur abruptly when  $e$  exceeds  $e_c$ , and it may be thought that the experiment by Gremain and Myard<sup>2</sup> corresponds to this case.

As was stated by Oono *et al.*<sup>7</sup>, if the cross-over region from the linear stretching to non-linear stretching by an external force is broad, then  $e_c$  will be small and thus the abrupt change will occur at an early stage.

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