

The Curie Temperature of the Ferroelectric Superlattice Films with Surface Modification

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We examine the critical behaviour of a finite alternating ferroelectric superlattice based on the transverse Ising model within the framework of the mean-field approximation. The results indicate that the features of the phase diagrams can be greatly modified by changing the transverse Ising model parameters. The transition temperature of alternating superlattice is described as function of the inter- and intra-layer exchange interactions, the strength of the transverse field, the superlattice thickness and the polarizations. In addition, the effects of surface modification on finite superlattices are also studied.

Key words: Ferroelectrics; Phase Transitions; Curie Temperature.

1. Introduction

Ferroelectric superlattice films have attracted much attention due to their potential applications to various electronic devices, such as dynamic random access memory and ceramic capacitors [1–6]. Especially, the fabrication of superlattice materials constitutes a powerful method to control the crystal structure and ferroelectric properties artificially. As to the ferroelectric superlattices, their physical properties including the spontaneous polarization, the Curie temperature, and the dielectric susceptibility, differ dramatically from simple solids formed from the same ferroelectric materials. Their significant physical properties arouse people to devote much work to analyze the effects of the interfacial coupling on ferroelectric superlattices. Theoretically, the static properties including polarization, susceptibility, and pyroelectric coefficient have been studied for ferroelectric superlattice using Ginzburg-Landau phenomenological theory [7–10] and the transverse Ising model (TIM) [11–13]. Besides, by applying the mean-field approximation, Wang et al. investigated extensively the ferroelectric phase transition of the superlattices [14, 15]. Zhou et al. used the effective field theory with correlations to calculate the Curie temperature of ferroelectric superlattice formed from two alternating materials [16]. Kaneyoshi studied the phase diagrams of a transverse

Ising superlattice based on the decoupling approximation in the differential operator technique [17]. In most of these discussions of ferroelectric superlattice films, the phase diagrams are usually described in two ways: the relations between the Curie temperature and the surface exchange interaction J_S [18–22], as well as the Curie temperature and the surface transverse field Ω_S [23–25]. However, the effects of various parameters on the phase diagrams of TIM have not yet been addressed systemically.

In the present paper, we focus on the Curie temperature of ferroelectric superlattice by modifying the transverse Ising model parameters of the surface layer. The mean-field theory is employed and the equation for the Curie temperature is obtained. Numerical results are given for the dependence of the Curie temperature on the transverse field, the exchange interactions, the thickness of the superlattice, and the polarizations.

2. Model and Formalism

We consider a finite ferroelectric superlattice with alternative slabs. The Ising model in a transverse field within the framework of the pseudospin theory is applied. The Hamiltonian of the system is given by [14–19]

$$H = - \sum_i \Omega_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z, \quad (1)$$

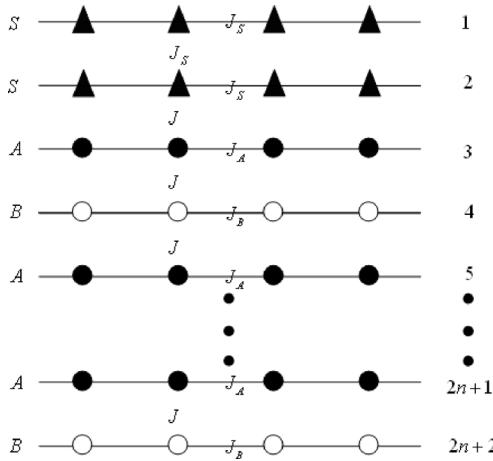


Fig. 1. Schematic illustration of finite ferroelectric superlattice modified with two surface layers.

where S_i^x and S_i^z are the x - and z -components of a spin- $\frac{1}{2}$ operator at site i , and J_{ij} is the two-pseudospin exchange interaction constant between the i th and j th site, where i and j run over only the nearest-neighbouring sites, Ω_i is the transverse field acting on the spin i or tunnelling constant, representing the ability of a proton in a hydrogen bond to tunnel from one site to the other. We consider a modified superlattice which alternates as SSAB...AB (Fig. 1) and assume that the superlattice has $N = 2n + 2$ layers. We consider different exchange interaction constants, with $J_{ij} = J_s$ and $\Omega_i = \Omega_s$ for the surface layers $N = 1, 2$. Layers $N = 3, 5, \dots, 2n + 1$ consist of atoms of type A with exchange interaction J_A and the transverse field is assumed to Ω_A , whereas layers $N = 4, 6, \dots, 2n + 2$ consist of atoms of type B with exchange interaction J_B and the transverse field is assumed to Ω_B . The exchange interactions between layers A and B are given by J .

Using mean-field approximation and assuming that the pseudospins in the same layer have the same values, the spin average along the z -direction, $\langle S_i^z \rangle$ can be written as [14–19]:

$$\langle S_i^z \rangle = (H_i^z / 2|H_i|) \tanh(|H_i| / 2k_B T), \quad (2)$$

where

$$H_i^z = 4J_{ij}\langle S_i^z \rangle + J_{i,i+1}\langle S_{i+1}^z \rangle + J_{i,i-1}\langle S_{i-1}^z \rangle, \quad (3)$$

$$|H_i| = \sqrt{\Omega_i^2 + (H_i^z)^2}. \quad (4)$$

$H(\Omega_i, 0, \sum_j J_{ij}\langle S_j^z \rangle)$ is the mean field acting the i th spin, k_B is the Boltzman constant, and T is the temperature.

When the temperature approaches the Curie temperature, the spin average tends to zero. Therefore, we can obtain a simple expressions from (2)–(4) for the finite alternating superlattice.

For the two surface layers, we have

$$\begin{aligned} \tau_S S_1 &= 4J_S S_1 + J_S S_2, \\ \tau_S S_2 &= 4J_S S_2 + J_S S_1 + J S_3 \end{aligned} \quad (5)$$

and for the alternating layers

$$\begin{aligned} \tau_A S_i &= 4J_A S_i + J(S_{i+1} + S_{i-1}), \quad (i = 3, 5, \dots, 2n+1), \\ \tau_B S_i &= 4J_B S_i + J(S_{i+1} + S_{i-1}), \quad (i = 4, 6, \dots, 2n+2), \end{aligned} \quad (6)$$

where S_i denotes $\langle S_i^z \rangle$, and

$$\begin{aligned} \tau_S &= 2\Omega_S \coth\left(\frac{\Omega_S}{2k_B T}\right), \quad \tau_A = 2\Omega_A \coth\left(\frac{\Omega_A}{2k_B T}\right), \\ \tau_B &= 2\Omega_B \coth\left(\frac{\Omega_B}{2k_B T}\right). \end{aligned} \quad (7)$$

Then, the following coefficient determinant equation can be obtained:

$$\det \begin{bmatrix} X_S & -C & & & \\ -C & X_S & -1 & & \\ & -1 & X_A & -1 & \\ & & -1 & X_B & -1 \\ & & & \ddots & \\ & & & -1 & X_A & -1 \\ & & & & -1 & X_B \end{bmatrix}_{(2n+2) \times (2n+2)} = 0, \quad (8)$$

where $X_S = \frac{(\tau_S - 4J_S)}{J}$, $X_A = \frac{(\tau_A - 4J_A)}{J}$, $X_B = \frac{(\tau_B - 4J_B)}{J}$, and $C = \frac{J_S}{J}$. We expand the equation above as

$$(X_S^2 - C^2)D_{2n} - X_S C_{2n-1} = 0, \quad (n \geq 2), \quad (9)$$

where the two determinants D_{2n} and C_{2n-1} are defined as:

$$\begin{aligned} D_{2n} &= \det \begin{bmatrix} X_A & -1 & & & \\ -1 & X_B & -1 & & \\ & -1 & X_A & -1 & \\ & & -1 & X_B & -1 \\ & & & \ddots & \\ & & & -1 & X_A & -1 \\ & & & & -1 & X_B \end{bmatrix}_{2n \times 2n}, \\ C_{2n-1} &= \det \begin{bmatrix} X_B & -1 & & & \\ -1 & X_A & -1 & & \\ & -1 & X_B & -1 & \\ & & \ddots & \\ & & & -1 & X_A & -1 \\ & & & & -1 & X_B \end{bmatrix}_{(2n+2) \times (2n+2)}. \end{aligned} \quad (10)$$

The solutions to (10) have been evaluated as in [18]:

$$D_{2n} = \frac{\sinh(n+1)\phi + \sinh(n\phi)}{\sinh \phi}, \quad (11)$$

$$C_{2n-1} = \frac{2 \sinh(n\phi)(\cosh \phi + 1)}{X_A \sinh \phi}$$

and here

$$2 \cosh \phi = X_A X_B - 2. \quad (12)$$

If $X_A X_B \leq 2$, then $\phi = i\theta$ and the hyperbolic functions become trigonometric functions of θ .

For $X_A X_B \leq 2$ the solution of (12) is $\theta = 2\pi / (2N + 1)$ and we have

$$X_A X_B - 2 = 2 \cos[2\pi / (2N + 1)]. \quad (13)$$

3. Results and Discussion

In order to facilitate the discussion, we take advantage of the definition of the ferroelectric dominant phase diagram (FPD) and the paraelectric dominant phase diagram (PPD), which are proposed by Teng and Sy [21, 22].

In Figure 2, we show the dependence of the Curie temperature of a finite ferroelectric superlattice on the thickness n . The Curie temperature increases as N increases. The Curie temperature of the superlattice reaches quite rapidly, and for $N \rightarrow \infty$, the bulk critical temperature of the infinite superlattice. Obviously, the Curie temperature of the finite superlattice for (a) is

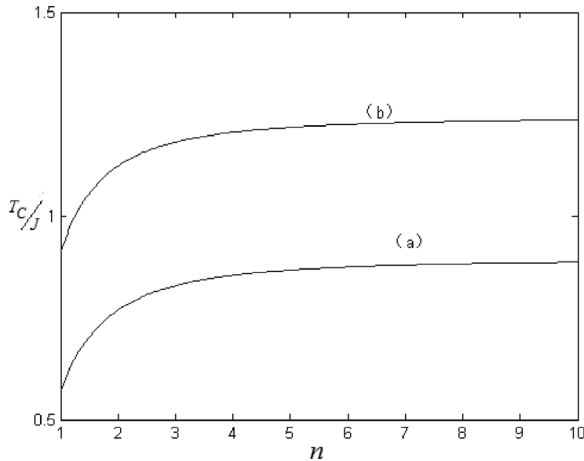


Fig. 2. Dependence of the critical temperature T_C on the thickness for $\Omega_A/J = 4$, $\Omega_B/J = 1$; (a): $J_A/J = 2$, $J_B/J = 0.5$; (b): $J_A/J = 0.5$, $J_B/J = 2$.

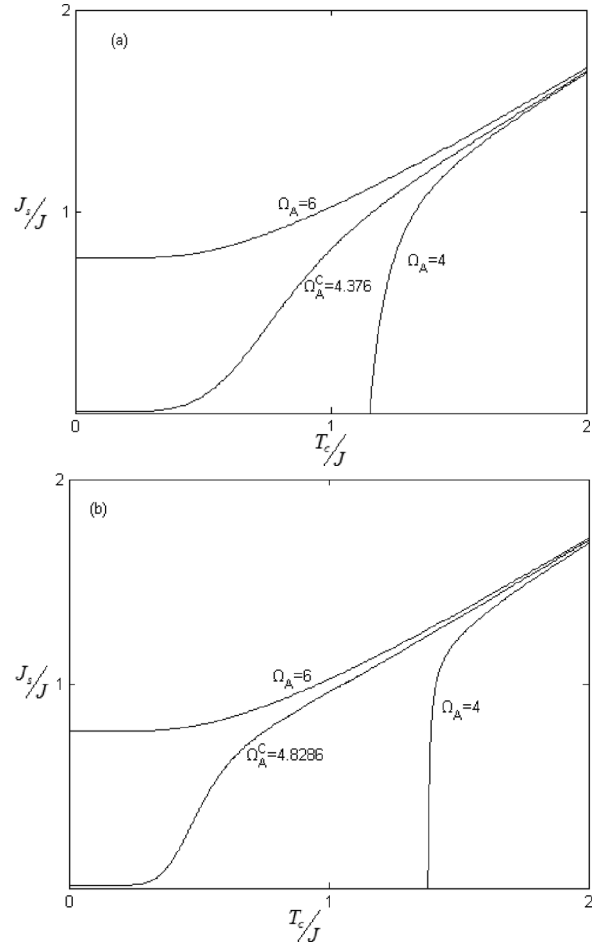


Fig. 3. Effect of Ω_A on the phase diagram ($\Omega_B > 2J_B$). All curves are for $\Omega_B/J = 3$, $J_A/J = 2$, $J_B/J = 1$, and $\Omega_s/J = 2$; (a): $N = 4$; (b): $N = 8$.

always less than that of the corresponding (b) and reaches the last one for large values of N . The main reason for this is that the exchange interaction J_B for (a) is larger than that of for (b) as the transverse field Ω_B is less than the transverse field Ω_A .

Figure 3 gives the phase diagrams between the Curie temperature and the exchange interaction on the surface, i.e. the curves of J_s versus T_C for different values of transverse field Ω_A . The larger the transverse field Ω_A , the larger the range of paraelectric phase; and the smaller the parameter Ω_A , the larger the range of ferroelectric phase. It is obvious that when Ω_A is less than the crossover value Ω_A^C , the phase diagram is in the ferroelectric dominant phase diagram (FPD), and now any J can result in a transition from ferroelectric to paraelectric phase with increasing the temper-

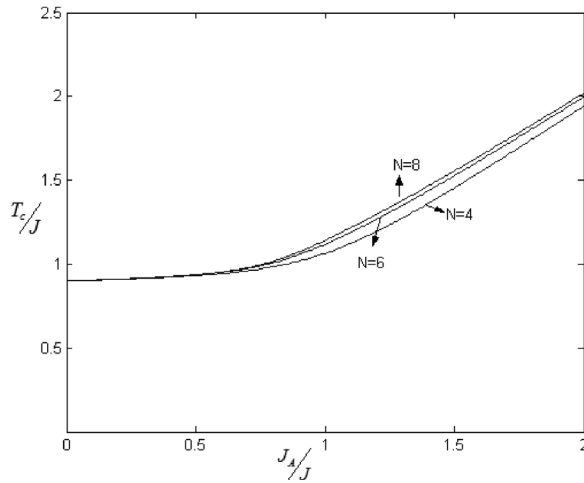


Fig. 4. Phase transition temperature of ferroelectric superlattice against the exchange interaction J_A/J for different layer-numbers. All curves are for $\Omega_S/J = 1.2$, $J_S/J = 0.8$, $\Omega_B/J = 3$, $J_B/J = 1.2$, and $\Omega_A/J = 2$.

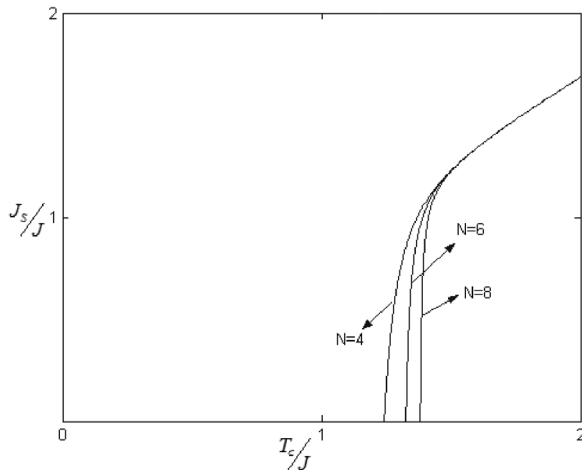


Fig. 5. Effect of layer-number N on the $J_S/J \sim T_c/J$ phase diagram. All curves are for $\Omega_A/J = 4$, $\Omega_B/J = 3$, $J_A/J = 2$, $J_B/J = 1$, and $\Omega_S/J = 2$.

ature. However, when Ω_A is larger than the value Ω_A^C , the phase diagram is in the paraelectric dominant phase diagram (PPD), and only larger J_S can result in a transition from ferroelectric to paraelectric phase with increasing the temperature. Figures 3a and b also reveal the effect of the lay number on the crossover value of the parameter Ω_A . The thicker the superlattice, the larger the crossover value Ω_A^C . Simultaneously, we find that large Ω_S will result in a larger range for the paraelectric state as well. In addition, the dependence of Ω_A on Ω_S is similar to that of Ω_B , and the dependence

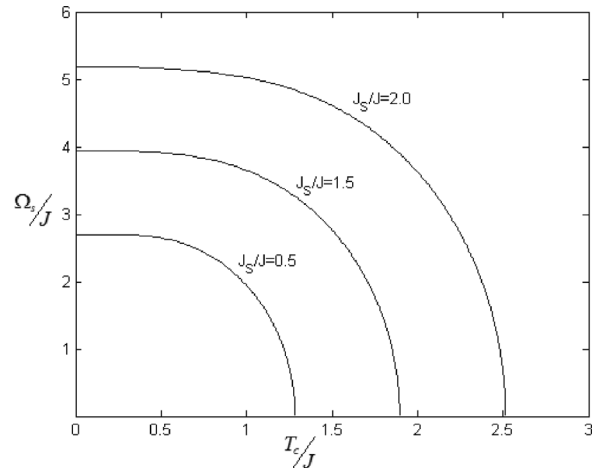


Fig. 6. Effect of J_S on the phase diagram. All curves are for $\Omega_A/J = 2$, $\Omega_B/J = 3$, $J_A/J = 0.5$, $J_B/J = 1$, and $N = 6$.

of Ω_B on the superlattice thickness is also similar to that of Ω_A , so we do not give a detailed discussion of these situations.

Figure 4 shows the dependence of the Curie temperature T_C/J on J_A for different layer-numbers. The Curie temperature increases considerably with the increase of J_A and the layer-number N . When J_A is large enough, The Curie temperature increases approximately linearly with the increase of J_A . Besides, the dependence of the Curie temperature T_C/J on J_B is likewise similar to that of J_A .

In Figure 5 we have plotted the critical temperature T_C versus J_S . The result is shown for cubic structure and for various number of layers. Note that the dependence of T_C on the layer thickness is significant only for small J_S and will not depend on the layer-number with the Curie temperature increasing. That is to say, while the Curie temperature is small, the thicker the superlattice, the larger range the ferroelectric phase; and the phase diagram will not depend on the thickness of the superlattice when the Curie temperature is large enough.

Figure 6 shows a graph of a maximum transverse field on the surface as a function of Curie temperature for different surface interaction J_S . We can see that with the increase of surface transverse field Ω_S , the transition temperature T_C falls from its maximum value. Otherwise, it indicates that the larger the ratio J_S/J , the larger the ferroelectric range in the phase diagram; the smaller the ratio J_S/J , the larger the paraelectric range in the phase diagram.

The local value of the polarization is proportional to the z -component of the pseudospin defined in (2) and satisfying (5) and (6) for the two-surface-layer ferroelectric superlattice, the polarization of the i th layer is

$$P_i = 2n\mu \langle S_i^z \rangle, \quad (14)$$

where n is the number of pseudospins in a unit volume. And we also define the mean polarization as

$$\bar{P} = \frac{1}{N} \sum_{n=1}^N P_i. \quad (15)$$

Physically, it is well known that studying the polarization is helpful for understanding the feature of the transition diagram. Therefore, we will investigate polarizations in the following work.

Figure 7 gives the temperature dependences of the polarizations for the superlattice film. For simplicity and without loss of generality, we consider the situation of a four-layer ferroelectric superlattice, and p_1 , p_2 , p_3 , and p_4 denote the polarization of the first layer (the surface), the second layer (the next surface), the third layer, and the fourth layer, respectively. It is obvious that there always exist the spontaneous polarization for p_1 , p_2 , p_3 , and p_4 irrespective of inter-layer correlation J . Meanwhile, it indicates that these polarizations depend sensitively on J . The larger the inter-layer correlation J , the larger the polarization for a fixed layer not only the surface layer but also the inner layer. Moreover, it is obvious that when J tends to zero,

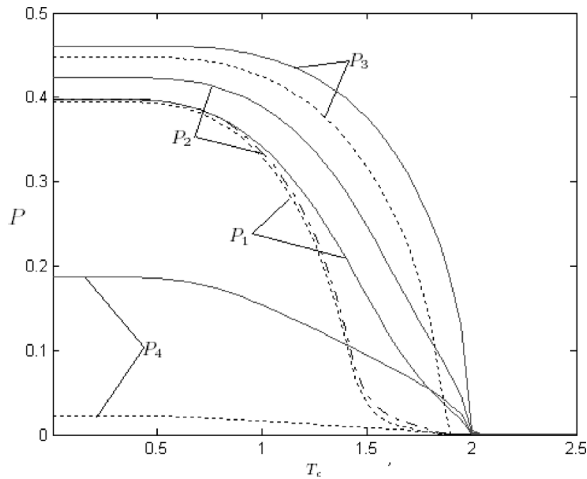


Fig. 7. Polarizations of the four-layer superlattice film. The solid lines are for $J = 1.0$ and the dashed lines are for $J = 0.1$. All curves are for $\Omega_S = 2.0$, $\Omega_A = 1.8$, $\Omega_B = 3.0$, $J_S = 1.3$, $J_A = 2.0$, and $J_B = 1.0$.

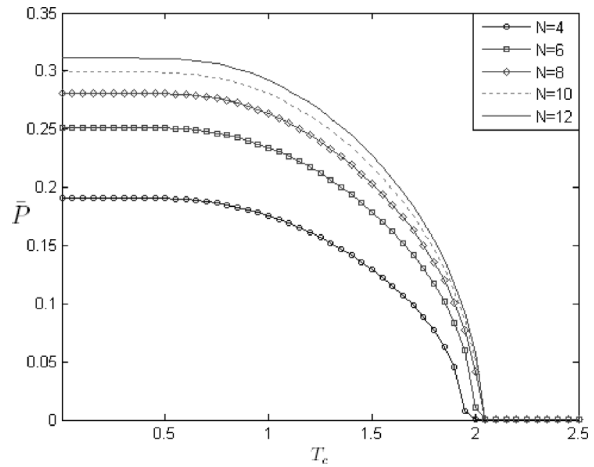


Fig. 8. Mean polarizations of the superlattice film for different layer-numbers. All curves are for $\Omega_S/J = 5.0$, $\Omega_A/J = 1.8$, $\Omega_B/J = 3.0$, $J_S/J = 1.3$, $J_A/J = 2.0$, and $J_B/J = 1.0$.

p_1 , p_2 , and p_3 always have spontaneous polarization, which is due to $\Omega_S \leq 2J_S$, $\Omega_A < 2J_A$ (i. e., $\Omega_S = 2.0$, $\Omega_A = 1.8$, $J_S = 1.3$, $J_A = 2.0$), but p_4 tends gradually to the paraelectric state, which is due to $\Omega_B > 2J_B$ (i. e., $\Omega_B = 3.0$, $J_B = 1.0$).

In addition, we find that the polarizations are $p_3 > p_2 > p_1 > p_4$ for a fixed J , the smallest polarization p_4 may be ascribed to the small exchange interaction J_B and the large exchange interaction J_A may result in the largest polarization p_4 physically. Obviously, the polarization of slab A is greater than that of slab B, which is attributed to the fact that the exchange interaction of slab A is larger than that of slab B. Furthermore, we find that the phase transition temperature (Curie temperature) depends sensitively on the exchange interactions J . The large exchange interaction J can result in a large phase transition temperature, i. e., the phase transition temperatures are approximately 1.9 and 2.0 for $J = 0.1$ and $J = 1.0$, respectively.

Figure 8 shows the numerical result for the mean polarization of the modified superlattice film on different layer-numbers. It can be seen from the figure that the mean spontaneous polarizations gradually increase with the increase of the layer-number N , and the increment of spontaneous polarization decrease remarkably. It also reveals the effect of the Curie temperature on the superlattice film thickness. The larger layer-number N , the larger is the value of the Curie temperature, which is in accordance with the result in Figure 2 above. Simultaneously, Figures 2 and 8 indicate that when the layer-number $N > 4$, the Curie tem-

perature just increase slightly with the increasing layer-number N .

4. Conclusion

In conclusion, we have considered the ferroelectric superlattice with surface modification. Using transverse Ising Model (TIM), we have studied the ferroelectric phase properties of a finite alternating superlattice described by the transverse Ising model. Meanwhile, the dependence of the transition temperature of ferroelectric films on the interface exchange constants, surface transverse field, and layer-number have been

calculated numerically. The method proposed here is simple for numerical calculations and expected to be able to study finite superlattices and impurity effects. We hope that these results may provide some useful information for theoretical and experimental work on ferroelectric superlattice with the developments of the experimental techniques in this field.

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