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## Relationship between direct and converse flexoelectric coefficients

Longlong Shu,<sup>1,2</sup> Fei Li,<sup>1</sup> Wenbin Huang,<sup>2</sup> Xiaoyong Wei,<sup>1,a)</sup> Xi Yao,<sup>1</sup> and Xiaoning Jiang<sup>2,b)</sup>

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Flexoelectric effect, as a universal electromechanical coupling, has drawn lots of interests in dielectric materials. However, due to the restrictions of present measurement techniques, only part of coefficients has been experimentally examined. In this study, we derived the coordinate-dependent Gibbs free energy density function in the inhomogeneous spatial field to investigate the relationship between the direct and converse flexoelectric coefficients. In crystalline mediums and systems, the direct and converse flexoelectric coefficients are proved to equivalent according to the Maxwell relation. These results will broaden the application of the Maxwell relation into non-linear spatial field, and provide the guideline for experimental measurement and prediction of flexoelectric coefficients. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4897647>]

### I. INTRODUCTION

Coupling between electrical and mechanical domains is one of the fundamental physical phenomena that underpin the functionality of a board range of materials and related devices. Specifically, electromechanical interactions varying from piezoelectric<sup>1,2</sup> coupling in the non-centrosymmetrical materials to electrostriction<sup>3,4</sup> coupling in all crystals without any symmetry constraints have been widely studied and applied in sensors, actuators, transducers, etc., over several decades. Recently, an inhomogeneous electromechanical effect, referred as flexoelectricity, has drawn considerable research interests both in fundamental analysis and experimental studies.<sup>5,6</sup> This somewhat understudied phenomenon is generally expressed in the form of<sup>7</sup>

$$P_l = \mu_{ijkl}^{dir} \frac{\partial S_{ij}}{\partial x_k} \text{ or } P_l = f_{ijkl}^{dir} \frac{\partial X_{ij}}{\partial x_k}, \quad (1)$$

where  $P_l$  is the induced polarization,  $\mu_{ijkl}^{dir}$  is the direct flexoelectric coefficient with respect to strain gradient, a fourth-rank tensor,  $S_{ij}$  is the strain and  $x_k$  is the axis of coordinate,  $f_{ijkl}^{dir}$  is the direct flexoelectric coefficient with respect to stress gradient, also a fourth-rank tensor, and  $X_{ij}$  is the stress.

The investigation regarding the flexoelectric effect was mainly focused on crystalline solid materials,<sup>7</sup> polymers,<sup>8</sup> liquid crystals<sup>9</sup> as well as biological materials such as biomembranes.<sup>10</sup> The concept of flexoelectricity in liquid crystals stems directly from the reorientation of irregularly shaped polarized molecules under strain gradients caused by splay- or bent-deformations, which is different from its cousin effect produced by uniform strain or stress, namely piezoelectric effect.<sup>11</sup> The first phenomenological model of flexoelectricity in solid dielectrics was proposed by Kogan.<sup>12</sup> However, in Kogan's original paper, he still used "piezoelectric effect" to describe this distinctive

electro-mechanical coupling effect caused by spatial derivative of strain. By comparing it with the similar phenomenon observed in liquid crystals, Indenbom suggested later that the term, "flexoelectric effect" should be adopted to describe this effect.<sup>13</sup> In principle, it is one of the fundamental properties of crystalline dielectric materials and should be present universally in all 32 point groups and 7 Curie groups due to its tensor nature as an even rank tensor, just like the electrostriction coefficients.<sup>14,15</sup> In principle, such tensor symmetry renders highly symmetrical materials, e.g., cubic and isotropic materials, to yield electric polarization under inhomogeneous mechanical field through the direct flexoelectric effect. This greatly enhances the feasibility of flexoelectric material as new and attractive sensing/actuating solid materials.<sup>16–18</sup> However, theoretical values of flexoelectric constants are estimated to be in the order of  $e/a$  ( $10^{-10}$  C/m), where  $e$  is the electronic charge and  $a$  is the crystal parameter.<sup>19,20</sup> For most bulk materials, flexoelectric coefficients are so small compared with piezoelectric constants, and thus, the relevant phenomena are always unperceivable and negligible in macro scale. In very recent years, enhanced direct flexoelectric effect was found in typical high permittivity ferroelectrics, which were in their paraelectric phase, thus excluding the piezoelectricity.<sup>21–23</sup> At the same time, the unpoled relaxor PMN-PT single crystals in the morphotropic phase boundary were also reported to have a large pure polarization when being bended.<sup>24</sup> Moreover, the micro/nano scale flexoelectric effect was proved to be extremely significant and hence broadened the application of flexoelectricity into thin films.<sup>25–28</sup> Intriguingly, some special designed heterogeneous thin films exhibited attractive physical phenomena in the aspects of strain gradient induced hysteresis loop shift and mechanical force induced polarization reversal, in response to the scaling effect of flexoelectricity.<sup>29–34</sup>

In crystalline medium, the strain gradient will result in the polarization, while on the other hand, the electric field gradient will result in mechanical strain, as schematically shown in Figs. 1(a) and 1(b), respectively. This effect is called the

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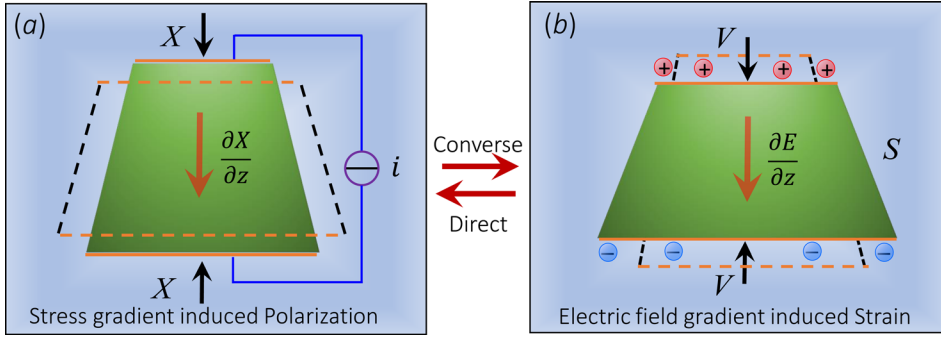


FIG. 1. (a) Schematic view of direct flexoelectric effect in a non-uniform spatial system. The electric current/polarization will be generated by the applied force gradient. (b) Schematic view of converse flexoelectric effect in a non-uniform spatial system. The mechanical stress/strain will be generated by the applied electric field gradient.

converse flexoelectric effect, and usually written in the tensor form as<sup>7,35,36</sup>

$$X_{ij} = \mu_{ijkl}^{con} \frac{\partial E_l}{\partial x_k} \text{ or } S_{ij} = f_{ijkl}^{con} \frac{\partial E_l}{\partial x_k}, \quad (2)$$

where  $E_l$  is the electric field,  $\mu_{ijkl}^{con}$  and  $f_{ijkl}^{con}$  are the converse flexoelectric coefficients, in response to direct flexoelectric coefficients  $\mu_{ijkl}^{dir}$  and  $f_{ijkl}^{dir}$ , respectively. However, compared with the direct flexoelectricity, both the experimental and theoretical investigation of the converse one is rather limited so far. Initial studies reported by Fu and Cross suggested that the strain yielded by the converse flexoelectricity was inevitably submerged by that of electrostriction effect due to the resolution limit of strain measurement techniques.<sup>35</sup> In this case, the thermodynamic relationship (Maxwell relation<sup>37</sup>) between the direct and converse flexoelectric coefficients, which is utmost importance for investigation, may provide theoretical guideline for the experimental converse flexoelectric measurement. It is well known that the previous application of Maxwell relation is concentrated on the spatial homogeneous system, wherein the physical variables, e.g., mechanical strain and electric field, are coordinate-independent in the whole system. In principle, taking temperature, mechanical strain, and electric field as independent variables, the differentiation of Gibbs free energy ( $G$ ) can be written as<sup>38</sup>

$$dG = -SdT - S_{ij}dX_{ij} - P_l dE_l, \quad (3)$$

where  $S$  (no subscript) and  $T$  (no subscript) refer to the entropy and temperature of the system, respectively. Note that this expression is in good agreement with most of the experimental situations except some extreme cases,<sup>39</sup> where additional variables should also be considered. However, for the flexoelectric effect, the existence of strain gradient as well as electric field gradient results in the coordinate-dependence of the mechanical strain and electric field so that the differentiation of Gibbs free energy  $G$  is not in the form of Eq. (3). In this study, we derived the Gibbs free energy density function in the general spatial inhomogeneous system, in order to examine the relationship between the direct and converse flexoelectric coefficients. This method will broaden the Maxwell relation into inhomogeneous spatial system.

## II. DIRECT AND CONVERSE FLEXOELECTRIC COEFFICIENTS

Note that in the crystalline material systems with respect to flexoelectricity, the electrical and mechanical variables

are always the functions of coordinates. Without loss of generality, we assume that the stress  $X_{ij}$ , strain  $S_{ij}$ , electric field  $E_l$ , and polarization  $P_l$  are the functions of the spatial coordinate axis  $x(x_1)$ ,  $y(x_2)$ , and  $z(x_3)$ . In light of the definition of stress-gradient-related flexoelectric coefficients  $f_{ijkl}^{dir}$ , temperature  $T$ , stress  $X_{ij}(x, y, z)$ , and electric field  $E_l(x, y, z)$  should be selected as independent variables. Therefore, the Gibbs free energy  $G(T, X_{ij}(x, y, z), E_l(x, y, z))$  can be used to derive the relationship between the direct and converse stress-gradient-related flexoelectric coefficients  $f_{ijkl}$ . In each volume infinitesimal,  $G(T, X_{ij}(x, y, z), E_l(x, y, z))$  can be written as

$$G(T, X_{ij}(x, y, z), E_l(x, y, z)) = \int \phi(T, X_{ij}(x, y, z), E_l(x, y, z)) dx dy dz, \quad (4)$$

where  $\phi(T, X_{ij}(x, y, z), E_l(x, y, z))$  is the volume density of Gibbs free energy. Take the differential of  $\phi(T, X_{ij}(x, y, z), E_l(x, y, z))$ , we obtain

$$d\phi(T, X_{ij}(x, y, z), E_l(x, y, z)) = -SdT - S_{ij}(x, y, z)dX_{ij}(x, y, z) - P_l(x, y, z)dE_l(x, y, z). \quad (5)$$

In order to simplify the analysis, we only consider the isolated process ( $dT=0$ ), and thus, Eq. (5) can be rewritten as

$$d\phi(X_{ij}(x, y, z), E_l(x, y, z)) = -S_{ij}(x, y, z)dX_{ij}(x, y, z) - P_l(x, y, z)dE_l(x, y, z). \quad (6)$$

In the crystalline materials and systems, the variation of the status function  $X_{ij}$ ,  $S_{ij}$ ,  $E_l$ , and  $P_l$  is continuous, rendering the differentiability of the Gibbs energy density  $\phi$ . For Eq. (6), take the partial differential of  $d\phi(X_{ij}(x, y, z), E_l(x, y, z))$  with respect to  $x_k$ . It is noticed that the value of  $x_k$  can stand for any one of the spatial coordinate axis  $x$ ,  $y$ , and  $z$ .

$$\begin{aligned} d \frac{\partial}{\partial x_k} \phi(X_{ij}(x, y, z), E_l(x, y, z)) &= d\phi'_{(x_k)}(X_{ij}(x, y, z), E_l(x, y, z)) \\ &= -\frac{\partial}{\partial x_k} S_{ij}(x, y, z)dX_{ij}(x, y, z) - \frac{\partial}{\partial x_k} P_l(x, y, z)dE_l(x, y, z) \\ &= -S'_{ij(x_k)}(x, y, z)dX_{ij}(x, y, z) - S_{ij}(x, y, z)dX'_{ij(x_k)}(x, y, z) \\ &\quad - P'_{l(x_k)}(x, y, z)dE_l(x, y, z) - P_l(x, y, z)dE'_{l(x_k)}(x, y, z). \end{aligned} \quad (7)$$

Here, we assume that the stress, electric field, and their respective gradients are independent variables, referring to Ref. 26. In this case, the status functions  $S'_{ij(x_k)}(x, y, z)$ ,  $S_{ij}(x, y, z)$ ,  $P'_{l(x_k)}(x, y, z)$ , and  $P_l(x, y, z)$  in Eq. (7) can be written as

$$S'_{ij(x_k)}(x, y, z) = -\frac{\partial\phi'_{(x_k)}(X_{ij}(x, y, z), E_l(x, y, z))}{\partial X_{ij}(x, y, z)}, \quad (8)$$

$$S_{ij}(x, y, z) = -\frac{\partial\phi'_{(x_k)}(X_{ij}(x, y, z), E_l(x, y, z))}{\partial X'_{ij(x_k)}(x, y, z)}, \quad (9)$$

$$P'_{l(x_k)}(x, y, z) = -\frac{\partial\phi'_{(x_k)}(X_{ij}(x, y, z), E_l(x, y, z))}{\partial E_l(x, y, z)}, \quad (10)$$

$$P_l(x, y, z) = -\frac{\partial\phi'_{(x_k)}(X_{ij}(x, y, z), E_l(x, y, z))}{\partial E'_{l(x_k)}(x, y, z)}. \quad (11)$$

According to the general definition in Eq. (1),  $f_{ijkl}^{dir}$  in each spatial coordinate position  $(x, y, z)$  can be expressed as

$$f_{ijkl}^{dir} = \frac{\partial P_l(x, y, z)}{(\partial X_{ij}(x, y, z)/\partial x_k(x, y, z))} \Big|_{E_l(x, y, z)}. \quad (12)$$

Subsequently, combined with Eq. (11), the direct flexoelectric coefficients can be formulated by taking the second derivatives of energy density of Gibbs free energy

$$f_{ijkl}^{dir} = -\frac{\partial^2\phi'_{(x_k)}(X_{ij}(x, y, z), E_l(x, y, z))}{\partial E'_{l(x_k)}(x, y, z)(\partial X_{ij}(x, y, z)/\partial x_k(x, y, z))} \Big|_{E_l(x, y, z)}. \quad (13)$$

According to the Maxwell relation, both the direct and converse flexoelectric coefficients can be interrelated by the reversal of the order of the differentiation. Hence, we obtain the relation

$$\begin{aligned} f_{ijkl}^{dir} &= -\frac{\partial^2\phi'_{(x_k)}(X_{ij}(x, y, z), E_l(x, y, z))}{(\partial X_{ij}(x, y, z)/\partial x_k(x, y, z))\partial E'_{l(x_k)}(x, y, z)} \Big|_{E_l(x, y, z)} \\ &= \frac{\partial S_{ij}(x, y, z)}{\partial E'_{l(x_k)}(x, y, z)} = f_{ijkl}^{con}. \end{aligned} \quad (14)$$

On the other hand, the relationship between the direct and converse strain-gradient-related flexoelectric coefficients  $\mu_{ijkl}$  can also be demonstrated by introducing Electric Gibbs free energy  $G_2$

$$G_2(S_{ij}(x, y, z), E_l(x, y, z)) = \varphi(S_{ij}(x, y, z), E_l(x, y, z))dx dy dz, \quad (15)$$

where  $\varphi(X_{ij}(x, y, z), E_l(x, y, z))$  is the Electric Gibbs free energy density, and its differentiation can be written as

$$\begin{aligned} d\varphi(X_{ij}(x, y, z), E_l(x, y, z)) &= X_{ij}(x, y, z)dS_{ij}(x, y, z) \\ &\quad - P_l(x, y, z)dE_l(x, y, z). \end{aligned} \quad (16)$$

Take the partial differential of  $d\varphi(X_{ij}(x, y, z), E_l(x, y, z))$  with respect to  $x_k$

$$\begin{aligned} d\frac{\partial}{\partial x_k}\varphi(X_{ij}(x, y, z), E_l(x, y, z)) &= d\phi'_{(x_k)}(X_{ij}(x, y, z), E_l(x, y, z)) \\ &= \frac{\partial}{\partial x_k}X_{ij}(x, y, z)dS_{ij}(x, y, z) - \frac{\partial}{\partial x_k}P_l(x, y, z)dE_l(x, y, z) \\ &= X_{ij}(x, y, z)dS'_{ij(x_k)}(x, y, z) + X'_{ij(x_k)}(x, y, z)dS_{ij}(x, y, z) \\ &\quad - P'_{l(x_k)}(x, y, z)dE_l(x, y, z) - P_l(x, y, z)dE'_{l(x_k)}(x, y, z). \end{aligned} \quad (17)$$

Finally, we obtain the relation

$$\begin{aligned} \mu_{ijkl}^{dir} &= -\frac{\partial^2\phi'_{(x_k)}(S_{ij}(x, y, z), E_l(x, y, z))}{(\partial S_{ij}(x, y, z)/\partial x_k(x, y, z))\partial E'_{l(x_k)}(x, y, z)} \Big|_{E_l(x, y, z)} \\ &= -\frac{\partial X_{ij}(x, y, z)}{\partial E'_{l(x_k)}(x, y, z)} = \mu_{ijkl}^{con}. \end{aligned} \quad (18)$$

### III. RESULTS ANALYSIS AND DISCUSSION

Based on above demonstration, the flexoelectric equation should be written as

$$I : P_l = f_{ijkl} \frac{\partial X_{ij}}{\partial x_k}, S_{ij} = f_{ijkl} \frac{\partial E_l}{\partial x_k}, \quad (19)$$

$$II : X_{ij} = -\mu_{ijkl} \frac{\partial E_l}{\partial x_k}, P_l = \mu_{ijkl} \frac{\partial S_{ij}}{\partial x_k}. \quad (20)$$

These two equations describe the flexoelectric effect in a more general way, suggesting the stress (strain) gradient converting into polarization and electric field gradient converting into strain (stress) was coupled by the value-identical flexoelectric coefficients. The minus sign in Eq. (20) illustrates that the existence of the electric field gradient results in the applied stress smaller than nominal situation when yielding the same strain, just like the minus sign in the piezoelectric equation when describing the piezoelectric stress constant.<sup>37</sup> Note that the subscript index combination from the fourth-rank tensor into a second-rank tensor will inevitably bring a factor of 2 or 1/2, when the subscript  $i$  is different with  $j$ . Therefore, we employ the full subscript form to clarify this relationship. Presently, the experimental results regarding the flexoelectric coefficients in crystalline materials are concentrated on direct  $\mu_{1111}$  and  $\mu_{1122}$ , namely longitudinal and transverse coefficients, respectively.<sup>40</sup> It is worth noting that compared with the well-known electro-mechanical couplings like piezoelectric and electrostrictive ones, the flexoelectric coupling is somewhat weak, even in some high permittivity perovskites. Consequently, the flexoelectric measurement requires high resolution as well as the high signal to noise ratio.<sup>7</sup> Based on the bending beam model<sup>15,41</sup> and the direct stress exerting on the trapezoid configuration,<sup>7</sup> coupling coefficients between the flexoelectric polarization and strain gradient were experimentally verified in the single crystals and ceramics as shown in Table I. Compared with

TABLE I. Recent experimental result on flexoelectricity in single crystal and ceramics.

Material	Direct ( $\mu\text{C}/\text{m}$ )			Converse ( $\mu\text{C}/\text{m}$ )		
	$\mu_{1111}$	$\mu_{1122}$	$\mu_{1212}$	$\mu_{1111}$	$\mu_{1122}$	$\mu_{1212}$
(Ba <sub>0.67</sub> Sr <sub>0.33</sub> )TiO <sub>3</sub> ceramic <sup>21,42,45</sup>	120	100	<u>110</u>	<u>120</u>	<u>100</u>	110
BaTiO <sub>3</sub> ceramic <sup>22</sup>	NA	50	NA	NA	50	NA
Ba (Ti <sub>0.87</sub> Sn <sub>0.13</sub> )O <sub>3</sub> ceramic <sup>23</sup>	NA	53	NA	NA	<u>53</u>	NA
PZT ceramic <sup>6</sup>	NA	1.4	NA	NA	<u>1.4</u>	NA
SrTiO <sub>3</sub> crystal <sup>41</sup>	$9 \times 10^{-3}$	$4 \times 10^{-3}$	$3 \times 10^{-3}$	<u><math>9 \times 10^{-3}</math></u>	<u><math>4 \times 10^{-3}</math></u>	<u><math>3 \times 10^{-3}</math></u>
PbMg <sub>0.33</sub> Nb <sub>0.67</sub> O <sub>3</sub> ceramic <sup>6</sup>	NA	3	NA	NA	<u>3</u>	NA
PMN-PT crystal <sup>24</sup>	NA	35	NA	NA	<u>35</u>	NA

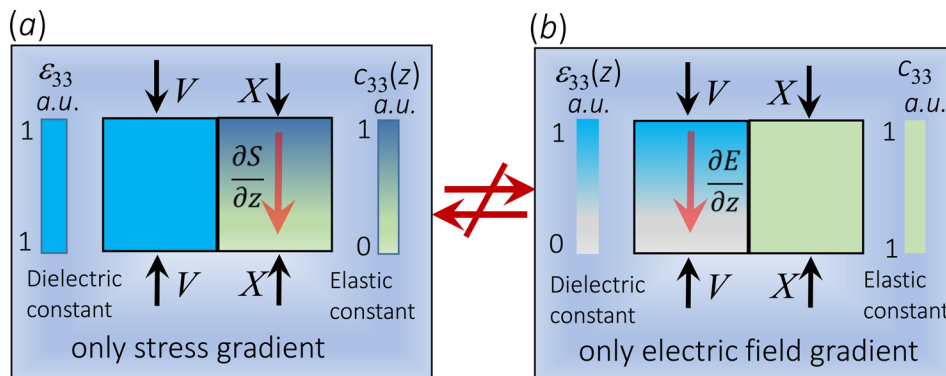


FIG. 2. (a) Schematic view of a material with the elastic constant  $c$  as a function of  $z$ . Only the mechanical stress/strain gradient will be generated when both applying electric voltage and mechanical force. (b) Schematic view of a material with the dielectric permittivity  $\epsilon$  as a function of  $z$ . Only the electric field gradient will be generated when both applying electric voltage and mechanical force.

the longitudinal and transverse coefficients, the shear component is hard to be measured because of the constrain of flexoelectric experimental measurement. Recently, the converse  $\mu_{1212}$  was successfully extracted by employing the AC voltage across the two lateral sides of the trapezoid sample.<sup>42</sup> Due to the Maxwell relation in crystalline materials and systems, we can predict the corresponding unexamined flexoelectric coefficients as shown in Table I. (underlined value). In this case, our derivation provides an effective way to estimate the flexoelectric coefficients, which are difficult to be determined by the present experimental measurement.

In some extreme situations, it is more convenient to generate mechanical stress gradient compared to electric field gradient, or vice versa. For example, in an ultrathin crystalline material as shown in Fig. 2(a), assume the elastic constant is continuously varied along coordinate  $z$ , the applied force results in a giant strain gradient, yielding a large electric polarization; while the applied voltage only results in a giant uniform electric field rather than an electric field gradient, rendering no converse flexoelectric response. On the other hand, in the ultrathin crystalline film as shown in Fig. 2(b), assuming the dielectric permittivity is a continuous function of coordinate  $z$ , the applied electric voltage results in a giant electric field gradient, yielding a large mechanical displacement; while the applied mechanical force only results in a giant uniform mechanical strain rather than a mechanical strain gradient, rendering no direct flexoelectric response. According to the thermodynamic relationship in non-uniform spatial field, it is possible to extract flexoelectric coefficients, irrespective of the absence of the strain

gradient or electric field gradient in some specialized materials and systems.

However, for those non-crystalline material systems, e.g., the newly developed quasiamorphous thin films,<sup>43,44</sup> the thermodynamic equilibrium derivation may not hold. This is because the physical variables and mechanical variables in non-crystalline material systems are not merely dependent on the spatial coordinate, but also dependent on the composition variation. It is possible that, in those materials and systems, the physical variables and mechanical variables in the volume infinitesimal are discrete, due to the composition variation. Consequently, the prerequisite of the differentiability of energy density will be unsatisfied so that the Maxwell relation cannot be applied to these cases.

#### IV. CONCLUSION

In conclusion, we demonstrated the fundamental relationship between the direct and converse flexoelectric coefficients by employing a coordinate-dependent Gibbs free energy density function in the non-uniform spatial field. The flexoelectric coefficients are derived to be equivalent through the Maxwell relation. This result could provide guideline for experimental measurement of flexoelectric coefficients, especially, when some of the coefficients are difficult to be measured.

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