

Crystal Period Vectors under External Stress in Statistical Physics (Version 2)

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A basic and general equation to determine period vectors (cell edge vectors) is necessary in physics, especially when crystals are under external stress. It has been derived in Newtonian dynamics. Since statistical physics should also generate such equation, we will provide a derivation. By extending the normal derivation for crystals under external pressure, regarding crystal cells as being filled with continuous media, formulating the work done by the external stress on the crystal explicitly, and deriving the forces on the surfaces of the cells by the external stress, we arrived at the equation for the period vectors, which is in principle the same as the above mentioned counterpart achieved in Newtonian dynamics. Everything also restores when the external stress reduces to the special case of external pressure. It should be applicable when crystals are under different pressures in different directions, like in piezoelectric and piezomagnetic phenomena.

Equations to determine the discrete particle positions and the period vectors (cell edge vectors $\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}$, forming a right-handed system) of crystals are needed in the prediction of their structures in equilibrium states. Since the inside particles (atoms, ions, electrons) always obey Newton's second law or the Schrodinger equation, the only unknown is the equation for the period vectors, especially when crystals are under external stress. It has been derived in the framework of Newtonian dynamics in recent years[1, 2]. We will derive it in statistical physics as follows.

First, let us recall the well-established way to do it for crystals under external pressure P . As the external pressure only acts on the surfaces of a macroscopic crystal bulk, this can be equivalently described as the action on the surfaces of a crystal cell. Then the work done by the pressure on a crystal cell is normally written as

$$dW = -PdV, \quad (1)$$

where the cell volume $V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$ is the conjugate variable of the pressure. Actually this work expression is further based on the idea that the cell is equivalently regarded as being filled with continuous media. Then the pressure can be calculated as equation (2.96) in the statistical reference book[3]:

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}, \quad (2)$$

where $\beta = 1/(kT)$, and Z , k , and T are the partition function, Boltzmann constant, and temperature respectively. This is essentially the general equation of the state of an equilibrium system under external pressure. As $dV = \sigma_a \cdot d\mathbf{a} + \sigma_b \cdot d\mathbf{b} + \sigma_c \cdot d\mathbf{c}$, where $\sigma_h = \partial V / \partial \mathbf{h}$ is the surface area vector of the cell with respect to \mathbf{h} , e.g.

$\sigma_a = \mathbf{b} \times \mathbf{c}$, the above work can also be written as

$$dW = -(P\sigma_a) \cdot d\mathbf{a} - (P\sigma_b) \cdot d\mathbf{b} - (P\sigma_c) \cdot d\mathbf{c}, \quad (3)$$

where $d\mathbf{h}$ is now the conjugate variable of the force $-P\sigma_h$ acting on the cell surface σ_h . Then we have

$$P\sigma_h = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (4)$$

which is in the form of determining the period vectors specifically. Combining Eq.(2) and Eq.(4) leads to $PV = kT(\partial \ln Z / \partial V)V = kT(\partial \ln Z / \partial \mathbf{a}) \cdot \mathbf{a} = kT(\partial \ln Z / \partial \mathbf{b}) \cdot \mathbf{b} = kT(\partial \ln Z / \partial \mathbf{c}) \cdot \mathbf{c}$. This means that the cell shape must show and keep certain symmetries for external pressure. Under such circumstances, Eq.(4) for any specific period vector, e.g. $\mathbf{h} = \mathbf{a}$, should be equivalent to Eq.(2) and about one-third calculation work of Eq.(2).

Now let us consider crystals under external stress Υ , a second-rank tensor (3×3 matrix). Since the force acting on the cell surface σ_h of the equivalent continuous media is $\Upsilon \cdot \sigma_h$ by the stress and the displacement of the cell surface is $d\mathbf{h}$, the work done by the stress should be

$$dW = (\Upsilon \cdot \sigma_a) \cdot d\mathbf{a} + (\Upsilon \cdot \sigma_b) \cdot d\mathbf{b} + (\Upsilon \cdot \sigma_c) \cdot d\mathbf{c}, \quad (5)$$

which becomes Eq.(1) when the stress reduces to the pressure $\Upsilon = -P\mathbf{I}$ with \mathbf{I} being an identity tensor. Since $d\mathbf{h}$ is the conjugate variable of the force $\Upsilon \cdot \sigma_h$ acting on the cell surface σ_h , we arrived at

$$\Upsilon \cdot \sigma_h = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (6)$$

which has the same form on the right side as that in Eq.(4). However, this is for crystals under external stress. Eq.(6) also shows that the period vectors can change independently of each other, with no additional restriction on the cell shape. For the special (pressure) case $\Upsilon = -P\mathbf{I}$, Eq.(6) reduces to Eq.(4), then reduces to Eq.(2), as it should.

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In classical statistics, as in equations (3.45-3.47) in the reference book[3], the partition function can be factorized as

$$Z = Z_k Z_u, \quad (7)$$

where Z_k and Z_u are the contributions of the kinetic energy E_k and potential energy E_p respectively as

$$Z_k = \frac{V^N}{N!} \int \frac{1}{h^{3N}} e^{-\beta E_k(\mathbf{p})} d\mathbf{p}, \quad (8)$$

where N is the number of total particles in the cell and the integration is over all particles' momentum spaces, and

$$Z_u = \frac{1}{V^N} \int e^{-\beta E_p(\mathbf{q})} d\mathbf{q}, \quad (9)$$

where the integration is over all particles' coordinate spaces. Bringing Eqs.(7, 8, and 9) into Eq.(6), we get

$$\Upsilon \cdot \sigma_h = -\frac{1}{V} NkT\sigma_h - \frac{1}{\beta} \frac{\partial \ln Z_u}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \quad (10)$$

The last term $-\partial \ln Z_u / (\beta \partial \mathbf{h})$ in this equation is essentially the same as the middle term $\partial E / \partial \mathbf{h}$ of equation (16) in our previous work [2], if the same way of derivation as in the second half of page 135 of the reference book[3] is taken.

As a result, although the kinetic energy term may be interpreted differently, all the rest are verified between the equation achieved in statistical physics here and that

previously derived based on the above mentioned pure Newtonian dynamics[1, 2]. Both can be further combined with quantum mechanics and should play roles in studying the very interesting piezoelectric and piezomagnetic effects.

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