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Crystal Period Vectors under External Stress in Statistical Physics (Version 3)

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In crystal periodic structure prediction, a general equation is needed to determine the period vectors (cell edge vectors), especially when crystals are under arbitrary external stress. It has been derived in Newtonian dynamics years ago, which can be combined with quantum mechanics by further modeling. Here we derived such an equation in statistical physics, applicable to both classical physics and quantum physics by itself.

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 particles (atoms, ions, electrons) inside crystals 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 general external stress. It has been derived in the framework of Newtonian dynamics in recent years[1, 2], which can be combined with quantum physics by further modeling. Here we will derive it in statistical physics, applicable to both classical physics and quantum physics by itself.

As a matter of fact, in statistical physics, the theory for the same purpose but for crystals under external pressure P, a special case of stress, has been well established for many years[3]. Let us start by recalling it briefly.

As crystals are made of periodic arrangements of the same cells in the three-dimensional space, they can be studied by focusing on one cell interacting with the rest cells. Thus, the external pressure actually only acting on the surfaces of a macroscopic crystal bulk can be equivalently described as the action on the surfaces of a crystal cell being studied. The work done by the pressure on a crystal cell is normally written as

$$dW = -PdV, \tag{1}$$

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

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}, \tag{2}$$

where $\beta = 1/(kT)$, and Z, k, and T are the partition function, Boltzmann constant, and temperature respectively. This is essentially the equation of the state of an equilibrium crystal under external pressure. In other words, the crystal cell volume and then the period vectors can be calculated based on this equation for the given external pressure.

Now let us change the forms of these equations slightly. 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

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

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

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

which is in the form of determining the period vectors specifically. Combining Eq.(2) and Eq.(4) leads to

$$\begin{aligned} PV &= kT(\partial \ln Z/\partial V)V = kT(\partial \ln Z/\partial \mathbf{a}) \cdot \mathbf{a} \\ &= kT(\partial \ln Z/\partial \mathbf{b}) \cdot \mathbf{b} = kT(\partial \ln Z/\partial \mathbf{c}) \cdot \mathbf{c}. \end{aligned}$$

This means that the cell shape must be assumed to show and keep certain symmetries for external pressure in actual calculation. 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 arbitrary external stress $\boldsymbol{\Upsilon}$, a second-rank tensor (3×3 matrix), to which neither Eq.(2) nor Eq.(4) can apply. Since the force acting on the cell surface σ_h of the equivalent continuous medium is $\boldsymbol{\Upsilon} \cdot \sigma_h$ by the stress and the displacement of the cell surface is $d\mathbf{h}$, the work done by the stress on the crystal cell is

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

which becomes Eq.(1) when the stress reduces to the pressure $\boldsymbol{\Upsilon} = -P\mathbf{I}$ with $\mathbf{I}$ being an identity tensor. Since, as shown in Eq.(5), $d\mathbf{h}$ is the conjugate variable of the force $\boldsymbol{\Upsilon} \cdot \sigma_h$ acting on the cell surface σ_h, based on the principles of statistical physics again, we arrived at

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

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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, for given external stress, the period vectors can be determined independently with each other, with no additional restrictions on the cell symmetry. For the special (pressure) case $\boldsymbol{\Upsilon} = -P\mathbf{I}$, Eq.(6) reduces to Eq.(4), then reduces to Eq.(2), as it should.

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

$$Z = Z_k Z_u, \tag{7}$$

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

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

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

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

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

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

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, in classical physics, although the kinetic energy term may be interpreted differently in details, all the rest are verified between the equation achieved in statistical physics here and that previously derived based on the Newtonian dynamics[1, 2].

Since elasticity theory is also about the action of external stress on crystals, it is better to compare it with this work.

First of all, elasticity theory studies crystals as continuous media essentially, then is not interested in crystal period vectors in principle. This work uses continuous media only when formulates the work done by the external stress, and tries to derive equation for determining the period vectors as the sole purpose. Whatever, let us suppose elasticity theory also studies microscopic structure of crystals.

Second, elasticity theory normally employs a reference state under no external stress, in which the period vectors $\mathbf{h}_0 = \mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0$, and all the particle position vectors $\mathbf{r}_{i,0} (i = 1, \cdots, N)$ in the center cell are supposed known. This work only tries to do something in the current state, completely forgetting all other states. In other words, this work treats every state independently essentially.

Third, it is well known that elasticity theory almost always uses the strain $\mathbf{u}$, also a second-rank tensor, to describe crystal deformation caused by the external stress. By definition, strain means an assumption that all the period vectors and particle position vectors of the current state under certain external stress are linearly related to the corresponding ones of the reference state in the same form:

$$\begin{aligned} \mathbf{h} &= \mathbf{h}_0 + \mathbf{u} \cdot \mathbf{h}_0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), & (11) \\ \mathbf{r}_i &= \mathbf{r}_{i,0} + \mathbf{u} \cdot \mathbf{r}_{i,0} \quad (i = 1, \cdots, N), & (12) \end{aligned}$$

as this rule applies to any point of the crystal. However this work does not make such an assumption, but regards and uses all the period vectors ($\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}$) and the particle position vectors $\mathbf{r}_i (i = 1, \cdots, N)$ as independent variables with each other, then any new crystal structure may be created by external stress and/or temperature. Typically, external stresses may cause structural phase transitions in crystals. Again since it is also well-known about how to determine the particle position vectors either by applying Newton's second law or the Schrodinger equation, this work only focuses on how to determine the period vectors.

Furthermore, elasticity theory employs (extended) Hooke's law as a basic principle, with some additional coefficients introduced, which may be determined by experiments. This work does not assume any analytical relationship between crystal period vectors and the external stress. Actually, Eq.(6) is the relationship between them, but with no additional coefficients introduced. Then Eq.(6) can be used to calculate the coefficients in Hooke's law, if the law applies.

In summary, Eq.(6) was derived here for determining crystal period vectors, then predicting crystal structures, by formulating the work done by the external stress on the crystal explicitly and applying the statistical principles. While the previously derived one in the frame work of Newtonian dynamics can be combined with quantum mechanics by further modeling, Eq.(6) applies to both classical physics and quantum physics by itself.

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