Crystal Period Vectors under External Stress in Statistical Physics (Version 5)

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In crystal periodic structure prediction, a basic and general equation is needed to determine their period vectors (cell edge vectors), especially under arbitrary external stress. It was derived in Newtonian dynamics years ago, which can be combined with quantum physics by further modeling. Here a new and concise approach based on the principles of statistical physics was employed to derive it into a new form, then applicable to both classical physics and quantum physics by its own. The new form also turned out to be the specific explicit equilibrium condition and the equation of state for crystals under external stress and temperature. This work was also compared with the elasticity theory.

I. INTRODUCTION

For predicting crystal structures, especially before being synthesized, the equations are needed to determine their discrete particle positions and their period vectors (cell edge vectors $\mathbf{h} = \mathbf{a}$, or $\mathbf{b}$, or $\mathbf{c}$, forming a right-handed system). 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 employ a new and concise approach based on the principles of statistical physics to derive it into a new form, then applicable to both classical physics and quantum physics by itself.

II. EXISTING THEORY FOR EXTERNAL PRESSURE

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 established firmly for long time[3]. Now let us recall it briefly.

A. The theory

From microscopic point of view, crystals are made of unlimited periodic arrangements of the same cells in the three-dimensional space. They can be studied by focusing on a "center" cell interacting with the rest cells. Then the external pressure, actually acting only on the surfaces of the macroscopic crystal bulk, can be equivalently described as the action on the surfaces of the crystal cell being focused on. The work done by the pressure on the cell is normally written as

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

where the cell volume $V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$. Actually this specific work expression can be better explained based on the idea that the cell is equivalently regarded as being filled with continuous medium. As the cell volume V is the conjugate variable of the pressure P, as shown in Eq.(1), based on the principle of statistical physics[6], the pressure can be derived as in equation (2.96) of 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 state of crystals under external pressure in equilibrium. In other words, the crystal cell volume can be calculated based on this equation for the given external pressure and temperature. However, it is not for the period vectors explicitly.

B. Expansion with respect to the period vectors

Now let us change 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 $d\mathbf{h}$ (=$d\mathbf{a}$, or $d\mathbf{b}$, or $d\mathbf{c}$) is now the conjugate variable of the force $-P\sigma_h$ acting on the cell surface σ_h. Then based on the principle of statistical physics, we have

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

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*Electronic address: `gl.cell@outlook.com` which is in the form of determining the period vectors specifically. Combining Eq.(2) and Eq.(4) leads to

$$PV = \frac{V}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{\mathbf{a}}{\beta}\cdot\frac{\partial \ln Z}{\partial \mathbf{a}} = \frac{\mathbf{b}}{\beta}\cdot\frac{\partial \ln Z}{\partial \mathbf{b}} = \frac{\mathbf{c}}{\beta}\cdot\frac{\partial \ln Z}{\partial \mathbf{c}}.$$

This means that the cell shape must be assumed to 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).

III. EQUATION DERIVATION FOR EXTERNAL STRESS

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. As said above, considering the focused crystal cell can be equivalently regarded as being made of continuous medium, the cell is now an actual object with matter in it everywhere, not simply a region of three-dimensional space. Then the force, described by the external stress, acting on the surface σ_h of the cell, is a real force and expressed as $\boldsymbol{\Upsilon}\cdot\sigma_h$. Further considering that the displacement of the cell surface is $d\mathbf{h}$, the work done by the external stress on the crystal cell is

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

This equation 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 principle of statistical physics again, we arrived at

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

It has the same form on the right side as that in Eq.(4). However, it is for crystals under external stress.

Supposing the period vectors are the only unknown variables for given external stress and temperature, then can be calculated by solving Eq.(6). During such procedure, different from the above external pressure case, as the period vectors are independent variables with each other, there should be no additional restrictions on the cell shape 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.

IV. DISCUSSION

A. Equation of state

In fact, Eq.(6) is an equation about the period vectors, all the particle position vectors in the cell, the external stress, and the temperature variables. In order to solve the whole crystal system, Eq.(6) must be combined with Newton's second law or the Schrodinger equation for motions of all particles in the cell. Since all particle motions can be solved by Newton's second law and/or the Schrodinger equation, for given period vectors as parameters, Eq.(6) can be used to solve the period vectors for given external stress and temperature and the solved particle motions. This process should be repeated till all variables converge. Since Newton's second law and the Schrodinger equation are fundamental principles of physics, which are always available and applicable, the whole procedure can be equivalently regarded as solving the period vectors by Eq.(6) for external conditions. Then Eq.(6) is the equation of state for crystals under external stress and temperature, in the form of the period vectors, instead of the cell volume.

As actually expressed by the period vectors, all kinds of crystal expansions caused by the change of the external stress or the temperature or both of them can be calculated by solving Eq.(6) under all external conditions concerned. Alternatively, as an example, supposing the temperature is fixed but the external stress is changed, one can do partial derivatives of Eq.(6) on both sides with respect to the changed components of the external stress respectively, then gets the isothermal expansion by the external stress.

As another example, let us consider the "isobaric" thermal expansion, in which the external stress is fixed but the temperature is changed. Actually, the particles' motion inside crystals is usually separated into the particles' equilibrium position motion and the harmonic oscillation around it. The harmonic oscillation can be represented by its frequency ω (or frequencies), which is a function of the period vectors and all particle equilibrium position vectors in the cell. For simplicity, let us suppose that there is only one particle in each cell, then its equilibrium position vector can always be set as zero, never changed. Then the partition function Z can be considered as a function of the frequency ω and temperature, when the temperature is changed, the right side of Eq.(6), $-kT\partial \ln Z(\omega, T)/\partial\mathbf{h}$, should change. Then the left side of Eq.(6), $\boldsymbol{\Upsilon}\cdot\sigma_h$, should also change. Since $\boldsymbol{\Upsilon}$ is fixed, σ_h should change, then so do the period vectors, which means that harmonic oscillation causes crystal thermal expansion.

For the special case of external pressure, as said above, the cell shape should keep certain symmetry, then the inside particle (equilibrium) positions should also assume so. Then if no structural phase transition happens, the crystal can only expand or contract uniformly. This means that the particle (equilibrium) position vectors and the period vectors should change proportionally, then all the particle (equilibrium) position vectors relative to the period vectors would not change. Then Eq.(6) is only about the period vectors, the external pressure, and the temperature variables, a pure traditional form of the equation of state.

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B. Internal stress and mechanical equilibrium condition

In 2010, Tuckerman expressed the crystal internal stress, also a second-rank tensor, as in Equation (5.6.9) of his statistical molecular simulation book[4], then applied it in a solid silicon system as an actual calculation example with a success[5]. In fact, this expression can also be written in the following way

$$\mathbf{P}^{(\mathrm{int})} = \frac{1}{\beta V} \sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}} \frac{\partial \ln Z}{\partial \mathbf{h}} \otimes \mathbf{h}. \tag{7}$$

Let us do three right dot products on Eq.(7) with the cell surface area vectors $(\sigma_a, \sigma_b, \sigma_c)$ separately and apply the relationship $\mathbf{h} \cdot \sigma_x = V \delta_{h,x}$, then

$$\mathbf{P}^{(\mathrm{int})} \cdot \sigma_h = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{8}$$

Bringing Eq. (8) into Eq. (6), then

$$\boldsymbol{\Upsilon} \cdot \sigma_h = -\mathbf{P}^{(\mathrm{int})} \cdot \sigma_h \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{9}$$

which is equivalent to

$$\boldsymbol{\Upsilon} + \mathbf{P}^{(\mathrm{int})} = 0, \tag{10}$$

as the three cell surface area vectors $(\sigma_a, \sigma_b, \sigma_c)$ are not in the same plane.

Since Eq.(10) means the internal and the external stresses balance each other, Eq.(6) is actually the "mechanical" equilibrium condition of the crystal under external stress and temperature, with the aid of the internal stress expressed by Eq.(7). The temperature appears in the partition function. Actually, it also means that Eq.(6) and the internal stress expression verified each other.

C. Comparison with elasticity theory

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

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, where N is the total number of particles in the cell. This work only tries to do something in the current state under any external stress, completely forgetting all other states. In other words, this work treats every state completely independently, with no information from any other state needed.

Third, elasticity theory, almost everywhere, uses the concept strain $\mathbf{u}$, also a second-rank tensor, to describe crystal deformation caused by the external stress. By definition, strain should mean 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:

$$\mathbf{h} = \mathbf{h}_0 + \mathbf{u} \cdot \mathbf{h}_0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{11}$$

$$\mathbf{r}_i = \mathbf{r}_{i,0} + \mathbf{u} \cdot \mathbf{r}_{i,0} \quad (i = 1, \cdots, N), \tag{12}$$

at least within a local macroscopic region of the crystal. Since Eqs.(11 and 12) restrict the crystal structure to change only linearly, then can not describe crystal structural phase transitions caused by the change of the external stress and temperature.

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 can describe any new crystal structure being created by the change of the external stress and/or temperature. Typically, external stress may cause structural phase transitions in crystals. Again since it is well-known about how to determine the particle position vectors by applying either Newton's second law or the Schrodinger equation, this work only focuses on how to determine the period vectors.

Furthermore, elasticity theory employs the generalized Hooke's law as a principle, in which the elastic constants were introduced and are usually determined by experiments. This work does not assume any analytical relationship between the crystal period vectors and the external stress. Actually, Eq.(6) is the temperature-dependent relationship between them, but with no additional constants or coefficients introduced, supposing everything in Eq.(6) can be at least calculated numerically. Then Eq.(6) can be used to calculate the elastic constants in the generalized Hooke's law, when the law applies, for given temperatures.

D. Classical physics

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

$$Z = Z_k Z_u, \tag{13}$$

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

$$Z_k = \frac{V^N}{N!}\int \frac{1}{h^{3N}} e^{-\beta E_k(\mathbf{p})} d\mathbf{p}, \tag{14}$$

where h is Planck constant, and the integration is over all particles' momentum spaces, and

$$Z_u = \frac{1}{V^N}\int e^{-\beta E_p(\mathbf{q})} d\mathbf{q}, \tag{15}$$

where the integration is over all particles' coordinate spaces in the cell. Bringing Eqs.(13, 14, and 15) into Eq.(6), we get

$$\boldsymbol{\Upsilon}\cdot\sigma_h = -\frac{1}{V}NkT\sigma_h - \frac{1}{\beta}\frac{\partial \ln Z_u}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{16}$$

The last term $-kT\partial \ln Z_u/\partial \mathbf{h}$ 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]. For "crystals" only containing ideal gases under external pressure, Eq.(16) becomes the ideal gas equation: $PV = NkT$.

V. 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. Since the period vectors are only meaningful in equilibrium states, where the external and the internal temperatures should be the same, Eq.(6) is not only the equilibrium condition, but also the equation of state for crystals under external stress and external temperature, expressed on the basis of the period vectors. Eq.(6) also concluded that harmonic oscillators can cause crystal thermal expansion. This work is different from the elasticity theory.

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[6] If the work done on a system can be written as in the form of $dW = A_1dB_1 + A_2dB_2 + \cdots + A_idB_i + \cdots$, for any pair of A_i and B_i variables, one has $A_i = -kT\partial \ln Z/\partial B_i$.