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Crystal Period Vectors under External Stress in Statistical Physics (Version 9)

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For crystal periodic structure prediction, a new and concise approach based on the principles of statistical physics was employed to derive a new form of the equation to determine their period vectors (cell edge vectors), under general external stress. Then the new form is applicable to both classical physics and quantum physics. It also turned out to be the equation of state and the mechanical equilibrium condition for crystals under external stress and temperature. It should be helpful in piezoelectric and piezomagnetic studies, as the period vectors were changed by the external stress. For linear elastic crystals, it is actually also the microscopic but temperature-dependent form of the generalized Hooke's law, then can be used to calculate the corresponding elastic constants of the law, for given temperatures.

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 $\mathbf{h} = \mathbf{a}$, $\mathbf{b}$, 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], 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 rigorously derive it into a new form, then applicable to both classical physics and quantum physics by itself. It also turned out to be the equation of state and the mechanical equilibrium condition for crystals under external stress and temperature. Later, the new form and the previously derived one will be shown to verify each other.

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, a special case of stress, has been established firmly for long time[2]. 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 "center" cell. The work done by the pressure P on the cell is normally written as

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

where the cell volume $V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$. 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[5], the pressure can be derived as in equation (2.96) of the statistical reference book[2]:

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

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 $dV = \sigma_{\mathbf{a}} \cdot d\mathbf{a} + \sigma_{\mathbf{b}} \cdot d\mathbf{b} + \sigma_{\mathbf{c}} \cdot d\mathbf{c}$, where $\sigma_{\mathbf{h}} = \partial V/\partial \mathbf{h}$ is the surface area vector of the cell with respect to $\mathbf{h}$, e.g. $\sigma_{\mathbf{a}} = \mathbf{b} \times \mathbf{c}$, the above work can also be written as

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

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

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

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

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

This means that the cell shape must be assumed and kept 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).

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) applies.

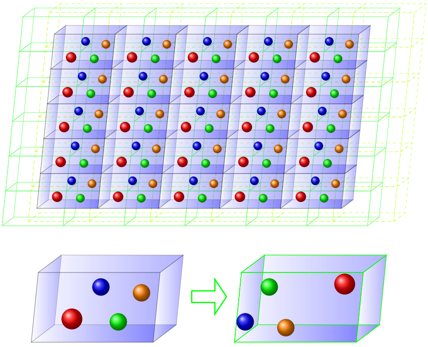

FIG. 1: While the positions of the particles inside a crystal are fixed, all the cells as a whole can be translated anywhere together, then placed in the new position, though only one layer of cells shown here. The green frame is an example of the new cell placement, and the lime frame of dashed lines is another. As a result, as shown in the lower part of this figure, the red biggest particle in the bottom-left corner of the old cell on the left, is in the top-right corner of the new green-framed cell on the right now, viewed through the front surfaces.

As shown in Fig. 1, while the positions of the particles inside a crystal are fixed, all the cells as a whole can be translated anywhere together, then be placed in the new position. The green and the lime frames in the figure are two example placements. All the translations should be equivalent to each other in physics, and also equivalent to the average of them. This can also be described as that while the cells are kept fixed, the particles are translated as a whole anywhere together. As a result, while all the relative positions between the particles are fixed, any individual particle can appear anywhere in the cell. The above-mentioned average of all the cell movements corresponds to the situation where the fixed cells are made of continuous medium. Then any cell is now an actual object with matter in it everywhere, instead of, as normally described, a vacuum region of three-dimensional space containing some discrete particles. As a matter of fact, any instance of all fixed cells with all fixed particle positions is one of the indistinguishable microscopic states discussed and averaged in our previous work[1]. Since the total mass of each cell is never changed, the cell surfaces become physical ones of fixed infinitesimal fraction of the cell mass in an extremely thin layer, from pure geometry planes. Then the force, described by the external stress, acting on the physical surface $\sigma_\mathbf{h}$ of the cell, is a real force and expressed as $\boldsymbol{\Upsilon}\cdot\sigma_\mathbf{h}$. Further considering that the displacement of the physical cell surface is $d\mathbf{h}$, the work done by the external stress on the crystal cell is

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

Then as seen, this equation was written rigorously based on the original definition of the work, where the subject of the displacement and the object being acted on by the corresponding force should be exactly the same actual object. Eq.(5) 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), the displacement $d\mathbf{h}$ is the conjugate variable of the force $\boldsymbol{\Upsilon}\cdot\sigma_\mathbf{h}$ acting on the physical cell surface $\sigma_\mathbf{h}$, based on the principle of statistical physics again, we arrived at

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

It has the same form on the right side as that in Eq.(4), except the plus/minus sign. However, it is for crystals under external stress, as shown on the left side.

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 completely independent variables with each other, there should be no additional restrictions on the cell shape symmetry (Eq.(2) does not apply). For the special (pressure) case: $\boldsymbol{\Upsilon} = -P\mathbf{I}$, Eq.(6) reduces to Eq.(4), then reduces to Eq.(2), as it should.

However, as a reminder, whatever the cell movement in Fig. 1 or their average being employed, the relative positions between particles should always be kept fixed, thus the interactions between them, the cell energy, the partition function and all other physical quantities are independent of the cell movements. One incorrect idea is that “if the average of all the cell movements is used, since any two particles can appear anywhere, their relative distance can be any value in the cell.”

IV. 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[3]. 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 $(\sigma_{\mathbf{a}}, \sigma_{\mathbf{b}}, \sigma_{\mathbf{c}})$ separately and apply the relationship $\mathbf{h} \cdot \sigma_{\mathbf{x}} = V\delta_{\mathbf{h},\mathbf{x}}$, then

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

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

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

which is equivalent to

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

as the three cell surface area vectors are not in the same plane.

Since Eq.(10) means that the internal and the external stresses balance each other, Eq.(6) is actually the specific explicit 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.

V. EQUATION OF STATE AND SYSTEM EXPANSION

In fact, Eq.(6) is an equation about the period vectors, all the particle position vectors in the “center” 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, for 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), $\boldsymbol{\Upsilon} \cdot \sigma_{\mathbf{h}}$, should also change. Since the external stress $\boldsymbol{\Upsilon}$ is fixed, $\sigma_{\mathbf{h}}$ should change, then so do the period vectors. This means that the harmonic oscillation causes crystal isobaric thermal expansion.

For the special case of external pressure, as said above, the cell shape should be kept certain symmetry, then the inside particle (equilibrium) positions should also be assumed accordingly. 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.

VI. WORK AND ENERGY IN QUASI-EQUILIBRIUM PROCEDURE

Considering at some time, the system is in an equilibrium state with the period vectors $\mathbf{a}_i$, $\mathbf{b}_i$, and $\mathbf{c}_i$, under certain external stress and temperature. Later the external stress and/or temperature change but very slowly, then the system changes accordingly and reaches a new equilibrium state of the period vectors being $\mathbf{a}_f$, $\mathbf{b}_f$ and $\mathbf{c}_f$. For every moment of this procedure, the system should be in an instantaneous equilibrium state, satisfying Eq.(6), then the whole procedure is a quasi-equilibrium one. Although almost all variables like external stress, temperature, the period vectors, the cell surface vectors, and all particle position vectors, may change, performing an integration of Eq.(5) from the initial state to the final state, we get the work done by the external stress for the whole procedure:

$$W = \int_{\mathbf{a}_i}^{\mathbf{a}_f} (\boldsymbol{\Upsilon}\cdot\sigma_{\mathbf{a}})\cdot d\mathbf{a} + \int_{\mathbf{b}_i}^{\mathbf{b}_f} (\boldsymbol{\Upsilon}\cdot\sigma_{\mathbf{b}})\cdot d\mathbf{b} + \int_{\mathbf{c}_i}^{\mathbf{c}_f} (\boldsymbol{\Upsilon}\cdot\sigma_{\mathbf{c}})\cdot d\mathbf{c}. \tag{11}$$

The internal energy of the system is the total energy of the center cell E_t. Further denoting the internal energies of the initial and the final states as $E_{t,i}$ and $E_{t,f}$, respectively, then the total heat needed by the system in the procedure can be expressed as

$$Q = E_{t,f} - E_{t,i} - W. \tag{12}$$

VII. DISCUSSION

A. Piezoelectricity and piezomagnetism

The fascinating piezoelectric and piezomagnetic phenomena are induced when the external pressure on crystals in one direction is changed while those in the other two directions not. Since the external stress is changed, according to Eq.(6), the equation of state, the period vectors should also be changed, then to employ Eq.(6) to calculate the changed crystal structure accurately would be very helpful in these studies.

B. Comparison with elasticity theory and the generalized Hooke's law

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 macroscopic shapes and properties of crystals mainly, thus regards crystals as continuous medium, then is not interested in crystal period vectors in principle. This work considers continuous medium for cells but only when formulates the work done by the external stress on the crystal cell, and derives 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 not being acted by any 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 should be 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, forgetting all other states completely essentially. In other words, this work studies any individual state completely independently, with no information from any other state needed.

Third, elasticity theory introduces and widely uses the concept strain $\mathbf{u}$, also a second-rank tensor, to describe crystal deformation caused by the external stress. By definition, strain means that for any point vector $\mathbf{x}$ of the matter in the current state, one has $\mathbf{x} = \mathbf{x}_0 + \mathbf{u}\cdot\mathbf{x}_0$, where $\mathbf{x}_0$ is the corresponding point in the reference state, at least within a local macroscopic region of the crystal. Then all the period vectors and particle position vectors in the same local region of the current state under certain external stress should be linearly related to the corresponding ones of the reference state in the same form:

$$\mathbf{h} = \mathbf{h}_0 + \mathbf{u}\cdot\mathbf{h}_0 \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{13}$$

$$\mathbf{r}_i = \mathbf{r}_{i,0} + \mathbf{u}\cdot\mathbf{r}_{i,0} \qquad (i = 1, \cdots, N), \tag{14}$$

as well. Since Eqs.(13 and 14) 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 neither use the strain concept nor make the assumption of Eqs.(13 and 14), 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 stress and strain are assumed linearly related by introducing the elastic constants, which 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) is the microscopic form of the generalized Hooke's law, for the situation where the period vectors and the external stress approximately change proportionally in reality. The elastic constants in the generalized Hooke's law can be calculated by solving Eq.(6) under a series of values of the external stress, for a given temperature.

C. Verification in classical physics

In classical statistics, as in equations (3.45-3.47) in the reference book[2], the partition function can be factorized as

$$Z = Z_k Z_u, \tag{15}$$

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

$$Z_k = \frac{V^N}{N!} \int \int \cdots \int \frac{1}{h^{3N}} e^{-\beta E_k(\mathbf{p})} d\mathbf{p}, \tag{16}$$

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

$$Z_u = \frac{1}{V^N} \int_V \int_V \cdots \int_V e^{-\beta E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})} d\mathbf{R}, \tag{17}$$

where the integration is over all particles position vectors: $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N\}$, limited in the cell.

Since the integration in Eq.(16) has nothing to do with the period vectors, the derivative

$$\frac{\partial \ln Z_k}{\partial \mathbf{h}} = \frac{N}{V}\frac{\partial V}{\partial \mathbf{h}} = \frac{N}{V}\sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{18}$$

But a little more patience is needed for Eq.(17), as the the cell potential energy E_p is a function of all the period vectors and all the particle position vectors $\mathbf{R}$. For every particle in the "center" cell, the position vector can be expanded with respect to the period vectors:

$$\mathbf{r}_i = r_{i,\mathbf{a}}\mathbf{a} + r_{i,\mathbf{b}}\mathbf{b} + r_{i,\mathbf{c}}\mathbf{c} \quad (i = 1, \cdots, N), \tag{19}$$

where $r_{i,\mathbf{h}}$, in the range of $[0, 1)$, can be calculated as

$$r_{i,\mathbf{h}} = \frac{1}{V}\mathbf{r}_i \cdot \sigma_{\mathbf{h}} \quad (i = 1, \cdots, N;\ \mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{20}$$

Let us perform a similar derivation as in the second half of page 135 of the reference book[2], then the integration regarding $\mathbf{r}_i$ in the cell but per unit volume

$$\begin{aligned} \frac{1}{V}\int_V \cdots d\mathbf{r}_i &= \int_V \cdots \frac{d\mathbf{r}_i}{V} \\ &= \int_0^1 \int_0^1 \int_0^1 \cdots dr_{i,\mathbf{a}} dr_{i,\mathbf{b}} dr_{i,\mathbf{c}} \\ &\qquad (i = 1, \cdots, N). \end{aligned} \tag{21}$$

Then the derivatives of Z_u with respect to the period vectors become only the derivatives of the cell potential E_p inside the integration:

$$\begin{aligned} \frac{\partial Z_u}{\partial \mathbf{h}} &= \int_0^1 \int_0^1 \int_0^1 \int_0^1 \int_0^1 \int_0^1 \cdots \int_0^1 \int_0^1 \int_0^1 \times \\ &\quad \frac{\partial}{\partial \mathbf{h}} e^{-\beta E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})} dr_{1,\mathbf{a}} dr_{1,\mathbf{b}} dr_{1,\mathbf{c}} \times \\ &\quad dr_{2,\mathbf{a}} dr_{2,\mathbf{b}} dr_{2,\mathbf{c}} \cdots dr_{N,\mathbf{a}} dr_{N,\mathbf{b}} dr_{N,\mathbf{c}} \\ &\qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \end{aligned} \tag{22}$$

Since that the dependency of $\mathbf{R}$ on the period vectors must be considered as in Eq.(19) now, the following derivatives should be separated as

$$\begin{aligned} \frac{\partial E_p}{\partial \mathbf{h}} &= \left.\frac{\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}{\partial \mathbf{h}}\right|_{\mathbf{R}} + \left.\frac{\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}{\partial \mathbf{h}}\right|_{\mathbf{a},\mathbf{b},\mathbf{c}} \\ &\qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \end{aligned} \tag{23}$$

where

$$\begin{aligned} \left.\frac{\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}{\partial \mathbf{h}}\right|_{\mathbf{a},\mathbf{b},\mathbf{c}} &= \sum_{i=1}^{N} \frac{\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}{\partial \mathbf{r}_i}\frac{\partial \mathbf{r}_i}{\partial \mathbf{h}} \\ &= \sum_{i=1}^{N} -\mathbf{F}_i r_{i,\mathbf{h}} \\ &= \sum_{i=1}^{N} -\mathbf{F}_i \frac{\mathbf{r}_i \cdot \sigma_{\mathbf{h}}}{V} \\ &= -\frac{1}{V}\sum_{i=1}^{N} (\mathbf{F}_i \otimes \mathbf{r}_i) \cdot \sigma_{\mathbf{h}} \\ &\qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \end{aligned} \tag{24}$$

where $\mathbf{F}_i$ is the net of all the forces acting on particle i, by any other particles in any cell, including its image particles. Employing Eqs.(22, 23, and 24), it follows

$$\begin{aligned} -\frac{\partial \ln Z_u}{\beta \partial \mathbf{h}} &= -\frac{1}{\beta Z_u}\frac{\partial Z_u}{\partial \mathbf{h}} \\ &= \frac{-kT}{Z_u V^N} \int_V \int_V \cdots \int_V \frac{\partial}{\partial \mathbf{h}} e^{-\beta E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})} d\mathbf{R} \\ &= \frac{1}{Z_u V^N} \int_V \int_V \cdots \int_V e^{-\beta E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})} \times \\ &\left(\left.\frac{\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}{\partial \mathbf{h}}\right|_{\mathbf{R}} - \frac{1}{V}\sum_{i=1}^{N} \mathbf{F}_i \otimes \mathbf{r}_i \cdot \sigma_{\mathbf{h}} \right) d\mathbf{R} \\ &\qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \end{aligned} \tag{25}$$

Bringing Eqs.(18 and 25) into Eq.(6), we get

$$\Upsilon \cdot \sigma_{\mathbf{h}} = -\frac{1}{V}NkT\sigma_{\mathbf{h}} - \frac{1}{\beta}\frac{\partial \ln Z_u}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{26}$$

For "crystals" only containing ideal gases under external pressure, Eq.(26) becomes the ideal gas equation: $PV = NkT$.

Now let us consider equilibrium states where

$$\ddot{\mathbf{h}} = 0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{27}$$

$$\ddot{\mathbf{r}}_i = 0 \quad (i = 1, \cdots, N). \tag{28}$$

Then the previously derived dynamical equation for the period vectors based on the Newtonian dynamics: Equation (27) in the paper[1], becomes

$$\begin{aligned} \Upsilon \cdot \sigma_{\mathbf{h}} &= -\frac{2}{3V}\sum_{i=1}^{N} \frac{1}{2} m_i \left|\dot{\mathbf{r}}_i\right|^2 \sigma_{\mathbf{h}} + \\ &\quad + \left.\frac{\partial E_p}{\partial \mathbf{h}}\right|_{\mathbf{R}} - \frac{1}{V}\sum_{i=1}^{N} (\mathbf{F}_i \otimes \mathbf{r}_i) \cdot \sigma_{\mathbf{h}} \\ &\qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \end{aligned} \tag{29}$$

where Equations (9, 17, 19, 25, and 26) in the paper[1] were employed, with m_i being the mass of particle i in the cell. The last term $-kT\partial \ln Z_u/\partial \mathbf{h}$ in Eq.(26) as shown in Eq.(25) is the averaged form of the last two terms $(\partial E_p/\partial \mathbf{h})|_{\mathbf{R}}$ and $-\sum_{i=1}^{N}\mathbf{F}_i\otimes\mathbf{r}_i\cdot\sigma_{\mathbf{h}}/V$ of Eq.(29), then essentially they are the same in physics.

Then, in classical physics, as the corresponding kinetic energy terms in the two equations are normally also regarded the same as each other, Eq.(26) achieved in statistical physics here and Eq.(29) previously derived based on the Newtonian dynamics[1] verified each other.

D. Combination with the previous work

The previously derived Equation (27) in the paper[1] for the period vectors based on the Newtonian dynamics is a dynamical equation, then can be used as an "algorithm" for solving the equilibrium states. Let us replace its internal stress with Tuckerman's expression, Eq.(7), then get

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}}=\left(\boldsymbol{\Upsilon}+\mathbf{P}^{(\mathrm{int})}\right)\cdot\sigma_{\mathbf{h}}\quad(\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}),\tag{30}$$

where $\alpha_{\mathbf{h},\mathbf{h}}$ is an equivalent mass, then can be chosen with any positive real number. Eq.(30) can be used as an "algorithm" for solving Eq.(6) in both classical physics and quantum physics.

In the Born-Oppenheimer approximation, ions and electrons in crystals are usually solved by Newtonian dynamics and quantum mechanics separately. Then the partition function of the whole system can be factorized accordingly, then Eq.(6) is the combination of classical physics and quantum physics.

VIII. A ONE-DIMENSIONAL SIMPLIFIED MODEL SYSTEM

In 2010, Ma and Tuckerman applied Eq.(10) (or equivalently Eq.(6)) in a solid silicon system as an actual calculation example with a success[4]. However, it is based on the density functional theory, and can not be repeated quickly from scratch. Anyhow, we like to present a much simplified one-dimensional example in pure classical physics below.

A. The model

The "crystal" is assumed consisted of particles in one fixed straight line only. The "period vectors" are now only one scalar variable, denoted as $a>0$, which is also the "cell volume", as the corresponding cell surface area vector is assumed as a unit vector along the line. Let f_{ext} be the external scalar force, described by the external stress, acting on the cell surface, also along the line. When $f_{ext}>0$, it pulls the system outwards, then is a pull force. If $f_{ext}<0$, it presses the system inwards, then is a press force.

Let us further assume that there is only one atom in each cell. Considering the periodicity of the system, the net force on any atom from all other atoms is always zero, then the atom in the center cell can always be assumed at the coordinate origin.

For simplicity, the kinetic energy of the center cell or the atom(s) in it is modeled as

$$E_k=\frac{3}{2}kT.\tag{31}$$

Only the Lennard-Jones (L-J) 12-6 potential but between any pair of atoms will be considered:

$$\varphi^{(L-J)}(r)=4\epsilon\left[\left(\frac{\lambda}{r}\right)^{12}-\left(\frac{\lambda}{r}\right)^{6}\right],\tag{32}$$

where r is the distance between the atoms, $\epsilon=3.500\times10^{-20}$J, and $\lambda=2.800$Å. Then the force on an atom at r by the atom at the origin is

$$\begin{aligned}f^{(L-J)}(r)&=-\frac{d}{dr}\varphi^{(L-J)}(r)\\&=\frac{4\epsilon}{r}\left[12\left(\frac{\lambda}{r}\right)^{12}-6\left(\frac{\lambda}{r}\right)^{6}\right].\end{aligned}\tag{33}$$

Based on Eq.(32), considering only one atom in the center cell, the total cell potential is half of the total potential between the cell and all the rest cells, as every single one belongs to both of the two interacting cells:

$$\begin{aligned}E_p^{(L-J)}(a)&=\frac{1}{2}\sum_{j=-\infty}^{\infty(j\neq0)}\varphi^{(L-J)}(ja)\\&=\sum_{j=1}^{\infty}4\epsilon\left[\left(\frac{\lambda}{ja}\right)^{12}-\left(\frac{\lambda}{ja}\right)^{6}\right].\end{aligned}\tag{34}$$

Then the total energy of the center cell is

$$E_t=E_k+E_p^{(L-J)}(a).\tag{35}$$

Bringing Eqs.(31 and 34) into Eq.(29), we get the equation for the period:

$$f_{ext}+\frac{kT}{a}+F_{L\to R}(a)=0,\tag{36}$$

where

$$\begin{aligned}F_{L\to R}(a)&=-\frac{d}{da}E_p^{(L-J)}(a)\\&=\frac{1}{2}\sum_{j=-\infty}^{\infty(j\neq0)}jf^{(L-J)}(ja)\\&=\sum_{j=1}^{\infty}jf^{(L-J)}(ja)\\&=\sum_{j=1}^{\infty}\frac{4\epsilon}{a}\left[12\left(\frac{\lambda}{ja}\right)^{12}-6\left(\frac{\lambda}{ja}\right)^{6}\right],\end{aligned}\tag{37}$$

which is actually the net force on the right half system by the left half, wherever the system is bisected.

Fig. 2 shows the force $f^{(L-J)}(r)$ via the atoms' distance r as in Eq.(33) with the red line, and the net force $F_{L\to R}(a)$ via the system period a, as in Eq.(37), with the blue line. The red line behaves as people expect. When the two atoms are approaching closely to each other, they repel each other with unlimited strength. When they are running away from each other, they attract each other but weakly and weakly. Actually, such force between two neighbour atoms is the first item of the force $F_{L\to R}(a)$, as shown in Eq.(37). Since the two lines are almost completely coincident, the rest terms in Eq.(37) decrease very rapidly.

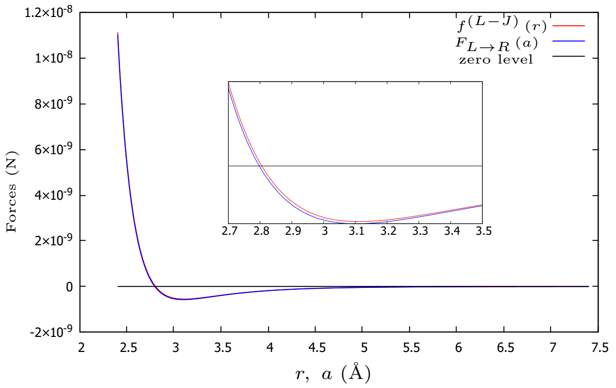

FIG. 2: The red line is the force on any atom by the atom in the center cell, as shown in Eq.(33); the blue line is the net force on the right half of the system by the left half when the system is bisected, as given in Eq.(37). As the data are very close, the two lines are almost completely coincident. The inside figure is an amplified one around the minimum forces.

Fig. 2 also shows that there is a minimum value in the force $F_{L\to R}(a)$. By taking, setting as zero, and solving it

$$\begin{aligned} &\frac{d}{da}F_{L\to R}(a) \\ =&\sum_{j=1}^{\infty}-\frac{4\epsilon}{a^2}\left[12\times13\left(\frac{\lambda}{ja}\right)^{12}-6\times7\left(\frac{\lambda}{ja}\right)^{6}\right] \\ =&\ 0, \end{aligned} \tag{38}$$

we get the value:

$$a_{min}=\lambda\left(\frac{\sum_{j=1}^{\infty}12\times13j^{-12}}{\sum_{j=1}^{\infty}6\times7j^{-6}}\right)^{\frac{1}{6}}=3.102\text{Å}. \tag{39}$$

When $a=a_{min}$, $F_{L\to R}(a)$ shows its the only-one minimum force $F_{L\to R}(a_{min})=-5.769\times10^{-10}$N.

Still in Fig. 2, when the period a runs from zero to a_{min}, the force $F_{L\to R}(a)$ decreases monotonically, and when the period a runs from a_{min} to the positive infinity, the force $F_{L\to R}(a)$ increases monotonically to the limit of zero. As a matter of fact, the system is not stable in the region $[a_{min},\infty)$. For simplicity, let us consider zero temperature for the region first. Since $F_{L\to R}<0$, Eq.(36) becomes

$$f_{ext}=-F_{L\to R}>0, \tag{40}$$

which means the external force has a pulling effect. Suppose the system is in an equilibrium state in the region. If any fluctuation factor results in $f_{ext}>|F_{L\to R}|$, the atoms should leave apart, then the period becomes bigger, then $|F_{L\to R}|$ decrease more, then more imbalance between f_{ext} and $|F_{L\to R}|$, then atoms should leave apart further, then the period becomes further bigger, then $|F_{L\to R}|$ decrease further more, then more imbalance between f_{ext} and $|F_{L\to R}|$, then atoms leave apart further further, till the system is broken. If the fluctuation factor results in $f_{ext}<|F_{L\to R}|$, a similar event will happen, however rather than system broken, the period should become smaller and smaller, leaving the region $[a_{min},\infty)$, then find an appropriate position in the region $(0,a_{min}]$ to set up a new equilibrium state. Regarding non-zero temperature, as the term kT/a is always positive as in the Eq.(36), essentially, it can not make the system to become more stable in the region $[a_{min},\infty)$.

Then first of all, we get the maximum pull force, which the system can endure, before being broken, as

$$f_{ext,max,pull}=|F_{L\to R}(a_{min})|=5.769\times10^{-10}\text{N}. \tag{41}$$

And let us do the following work only with the period in the region $(0,a_{min}]$.

However, as a comment, since the kinetic energy of the only one atom in the center cell is expressed as in Eq.(31), one may be worrying about how to keep the velocity of the mass center of the center cell as zero. This can be obtained by averaging all the states where the only difference is the atom's moving direction, with the same weight. An alternative description is to regard every two neighbour cells as one bigger cell. Then each bigger cell contains two same atoms, which can move in the opposite directions, and keep the mass center of the center cell being at rest. Essentially, this description is the same in physics as the model of one atom in each cell we adapt here, as Eqs.(36 and 37) apply to both.

Since constant volume is not much interesting, let us go for constant temperature and constant external force only.

B. Constant external temperature

Fig. 3 shows the changed system period by the changing external force, for three constant external temperatures. Supposing for the external force range from zero to 1.0×10^{-10}N, the period and the external force are assumed to change approximately linearly, the elastic constants of the Hooke's law, τ, can be calculated as in the following table: where a_0 is the period at which the ex-

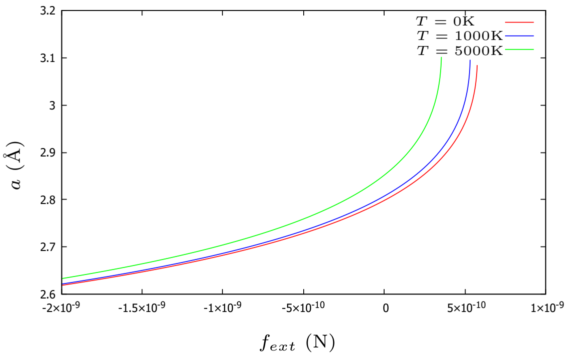

FIG. 3: Under constant temperatures at 0K, 1000K and 5000K respectively, the changing external force causes the system period changes.

T(K)	a_0(Å)	Δa(Å)	$\tau = \frac{\Delta f_{ext}}{\Delta a/a_0}$(N)
0	2.798	0.01949	1.436×10^{-8}
1000	2.807	0.02095	1.340×10^{-8}
5000	2.852	0.03027	9.422×10^{-9}

ternal force is zero, and $\Delta f_{ext} = 1.0 \times 10^{-10}$N. Then the Hooke's law can be expressed as

$$f_{ext} \approx \tau \frac{\Delta a}{a_0}. \tag{42}$$

In fact, the changing relationship between the period and the external force can also be calculated by taking the derivative of Eq.(36) with respect to the period.

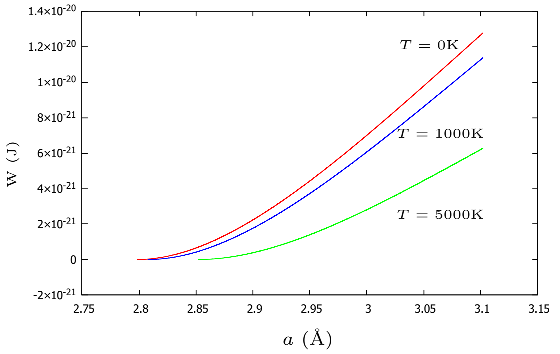

FIG. 4: Under three constant temperatures respectively, the work done by the external force in the quasi-equilibrium procedure from the state of zero external force to the state of a_{min}.

Employing Eq.(11) and choosing the state with the external force being zero and the state with the period being a_{min} as the initial and final ones respectively, the work done by the external force for the quasi-equilibrium procedure under the three constant temperatures can be calculated and shown in Fig. 4. Further using Eq.(12) and (35), the heat absorbed during this procedure is shown in Fig. 5.

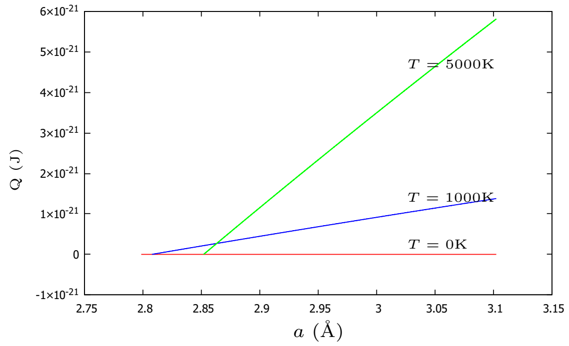

FIG. 5: Under the three constant temperatures respectively, the heat absorbed by the system in the quasi-equilibrium procedure from the state of zero external force to the state of a_{min}.

Fig. 5 shows that for zero temperature, no heat is needed by the system from outside. Imagining an object is running in a potential field of $E_p^{(L-J)}(r)$ with r as its position relative to the coordinate origin, as Eq.(34), it should experience the force acted by the field as $-dE_p^{(L-J)}(r)/dr$. According to the first equality of Eq.(37), that force is exactly the force $F_{L\rightarrow R}(a)$ for $r = a$. Further considering the force balance relationship of Eq.(40) for zero temperature, the quasi-equilibrium procedure in which the external force pulls the system period to increase is the same in physics as the procedure when one raises an object in a gravitational field with a force balancing the object's weight from a stationary state to another stationary state. In the latter procedure, the energy needed for the potential change is accurately compensated by the work done by the person who raised it, then no other energy exchange is needed. This is what is happening for zero temperature in Fig. 5. For non-zero constant temperatures, the system kinetic energy as shown in Eq.(31) is also fixed, then no change between the initial and the final states and no heat is needed for the kinetic energy. Furthermore, Eq.(36) means that the difference between the external force and the force $F_{L\rightarrow R}(a)$ is kT/a. See Fig. 5 again, the period a is in the range of $(2.8, 3.2)$, then kT/a is almost fixed as well. When an object in a gravitational field is raised up by an external force of fixed difference from its weight, the additional energy needed to compensate the potential change over the work done by the external force should be proportional to the object's height change. For the same reason, we see the heat lines in Fig. 5 are almost all straight ones for positive temperatures.

The heat can be exchanged between the system and an external heat reservoir through inelastic collisions between atoms of the system and particles of the external reservoir in its walls contacting with the system surfaces, when their temperatures are different.

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C. Constant external force

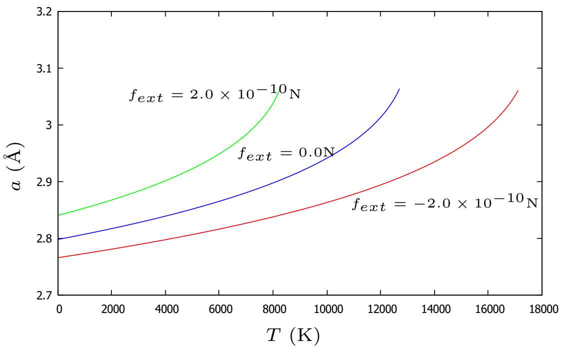

FIG. 6: Under three constant external forces respectively, the period is changed by the temperature.

Fig. 6 is the period changed by the temperature for three given external forces. Again based on Eq.(36), since the force $F_{L\to R}(a)$ has the unique minimum value at a_{min}, there is the upper limit

$$\begin{aligned} T_{max} &= -\frac{a_{min}}{k}\left(f_{ext} + F_{L\to R}\left(a_{min}\right)\right) \\ &= -2.247 \times 10^{13}\mathrm{K\,N^{-1}}\left(f_{ext} - 5.769 \times 10^{-10}\mathrm{N}\right), \end{aligned} \tag{43}$$

for the temperature. If the temperature is higher than T_{max}, the system can not exist any more. Then T_{max} is the melting point. In Fig. 6, all lines for various given external forces end at T_{max}. The figure also shows that the weaker pull force or the stronger press force, the higher melting point.

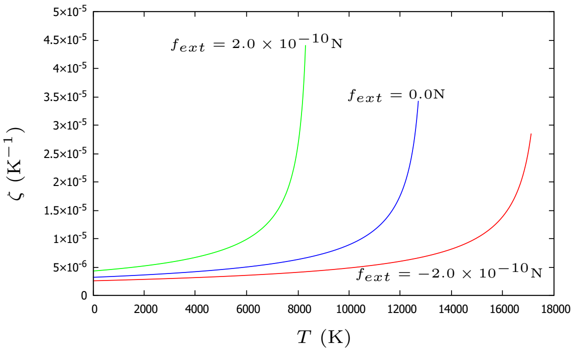

FIG. 7: Relative thermal expansion rate with temperature under the three given external forces.

If we take the derivative of Eq.(36) with respect to the period a under the constant external force, then get the relative thermal expansion rate as

$$\zeta = \frac{1}{a}\frac{da}{dT} = \frac{k}{a^2}\left(\frac{kT}{a^2} - \frac{d}{da}F_{L\to R}\left(a\right)\right)^{-1}, \tag{44}$$

which is shown in Fig. 7 for the three given external forces. Since as shown in Fig. 2, the force $F_{L\to R}(a)$ line is the flattest around the a_{min} value in the region $(0, a_{min})$ and essentially the temperature plays a very similar role as that the force $F_{L\to R}(a)$ plays in Eq.(36), Fig. 7 presents the top values of the relative thermal expansion rates, which means the system is very sensitive to the temperature, around the melting points.

The work done by the external force and the heat needed by the system for the quasi-equilibrium procedures under given external forces can also be calculated the same way as in the constant temperature case, however not presented here, as not much new physics observed. Anyhow, for this example, the FORTRAN 90 code can be obtained by sending emails to the author: gl.cell@outlook.com .

IX. SUMMARY

Eq.(6) was derived here for determining crystal period vectors, then predicting crystal structures, by rigorously formulating the work done by the external stress on the crystal 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. While verifying each other in classical physics, they can be combined.

It also turned out that Eq.(6) is not only the equilibrium condition, but also the equation of state for crystals under external stress and temperature, expressed on the basis of the period vectors. Furthermore, Eq.(6) is also the microscopic but temperature-dependent form of the generalized Hooke's law, for linear elastic crystals, then can be used to calculate the corresponding elastic constants of the law, for given temperatures. It should play an essential role in piezoelectric and piezomagnetic studies, caused by an increase of the external pressure on crystals but only in one direction, as well. At the end, the system stability, melting temperature, period changed by the external force and temperature, Hooke's law and thermodynamic properties and procedures were demonstrated in a one-dimensional simplified model.

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[5] If the work done on a system can be written as in the form of $dW = A_1 dB_1 + A_2 dB_2 + \cdots + A_i dB_i + \cdots$, for any pair of A_i and B_i variables, one has $A_i = -kT\partial \ln Z/\partial B_i$.