

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

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For crystals under external stress and temperature, a general equation to determine their period vectors (cell edge vectors) was derived based on the principles of statistical physics. This equation applies to both classical systems and quantum systems. It is consistent and can be combined with the previously derived one in the Newtonian dynamics. The existing theory for crystals under external pressure is covered as a special case. The new equation is also the mechanical equilibrium condition and the equation of state for crystals under external stress and temperature. It should be helpful in studying piezoelectric and piezomagnetic materials, since the period vectors change with external stress. For linear elastic crystals, it is the microscopic and temperature-dependent form of the generalized Hooke's law, therefore, it can be used to calculate the corresponding elastic constants, for given temperatures.

I. INTRODUCTION

For predicting crystal structures, especially before crystals are 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 Schrödinger 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 the 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 starting from the rigorous definition of work to derive a new equation. Since the derivation is based on the fundamental principles of statistical physics, the new equation applies to both classical systems and quantum systems by itself. It is consistent and can be combined with the previously derived one in the Newtonian dynamics. It also turned out to be the mechanical equilibrium condition and the equation of state for crystals under external stress and temperature. The existing statistical physics theory for external pressure is covered as a special case.

II. EQUATION DERIVATION FOR PERIOD VECTORS UNDER EXTERNAL STRESS

Consider crystals under external stress \mathbf{T} , a second-rank tensor (3×3 matrix), and at temperature T . From a microscopic point of view, crystals consist of unlimited periodic arrangements of identical cells in the three-dimensional space. They can be studied by focusing on a "center" cell interacting with all other cells. The exter-

nal force, which only exerts on the surfaces of the macroscopic crystal bulk, can be equivalently described as the action on the surfaces of the "center" cell.

For deriving the equation about the period vectors, we start with the formulation of the work done by arbitrary external stress on the crystal cell. In order to do it rigorously, let us bear in mind that in the definition of work, the subject of the displacement and the object being acted on by the corresponding force should be exactly the same physical object.

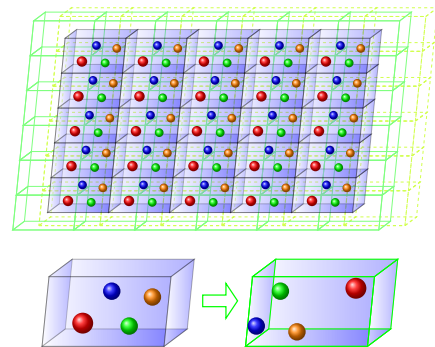


FIG. 1: If the positions of the particles in a crystal are fixed, all the cells can be translated anywhere together, though only one layer of cells is shown here. The green frame is an example of the new cell placement, and the lime frame of dashed lines is another. As shown in the lower figure, the red particle in the bottom-left corner of the amplified original cell on the left, is in the top-right corner of the amplified 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. The green and the lime frames in the figure are two new placements. In physics, all the translations are equivalent to each other, and equivalent to the average of all of them. Alternatively, if the cells are kept fixed, it can be described as

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that the particles are translated as a whole together to anywhere. As a result, while all the relative positions between the particles are fixed, individual particles can appear anywhere in the cell. The average of all the cell movements corresponds to the situation where the fixed cells are made of continuous medium. Therefore, 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. In fact, any instance of all fixed cells with all fixed particle positions is one of the indistinguishable microscopic states discussed in Section 4 of our previous work[1]. Since the total mass of each cell never changes, the cell surfaces become physical entities of a fixed, albeit infinitesimally small fraction of the cell mass, rather than pure geometric planes. For expressing the displacements and the forces acting on these actual surfaces, their area vectors are denoted as $\sigma_{\mathbf{a}} = \mathbf{b} \times \mathbf{c}$, $\sigma_{\mathbf{b}} = \mathbf{c} \times \mathbf{a}$, and $\sigma_{\mathbf{c}} = \mathbf{a} \times \mathbf{b}$ with respect to the period vectors $\mathbf{h} = \mathbf{a}$, \mathbf{b} , and \mathbf{c} separately. Then the force, described by the external stress Υ , acting on the physical surface $\sigma_{\mathbf{h}}$ of the cell, is a real force and expressed as $\Upsilon \cdot \sigma_{\mathbf{h}}$. The displacement of the physical cell surface $\sigma_{\mathbf{h}}$ is $d\mathbf{h}$ ($=d\mathbf{a}$, $d\mathbf{b}$, or $d\mathbf{c}$) as it represents a physical quantity. Then according to the definition, the work done by the external stress on the crystal cell is

$$dW = (\Upsilon \cdot \sigma_{\mathbf{a}}) \cdot d\mathbf{a} + (\Upsilon \cdot \sigma_{\mathbf{b}}) \cdot d\mathbf{b} + (\Upsilon \cdot \sigma_{\mathbf{c}}) \cdot d\mathbf{c}. \quad (1)$$

Since, as shown in Eq.(1), the displacement $d\mathbf{h}$ is the conjugate variable of the force $\Upsilon \cdot \sigma_{\mathbf{h}}$ acting on the physical cell surface $\sigma_{\mathbf{h}}$, based on the principle of statistical physics[5], we arrive at

$$\Upsilon \cdot \sigma_{\mathbf{h}} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (2)$$

where $\beta = 1/(kT)$, and k and Z are the Boltzmann constant and the system partition function respectively. The partition function is a function of the system energy and temperature. Eq.(2) can determine all the independent period vectors for crystals under external stress Υ and temperature T , if all other variables are known.

III. EXISTING STATISTICAL THEORY FOR EXTERNAL PRESSURE AS A SPECIAL CASE

In statistical physics, the theory for crystals under external pressure has been established for a long time[2]. Now let us re-derive the basic equations for this special case from the above formulae of general external stress to make sure their consistency.

For an external pressure P , the stress reduces to: $\Upsilon = -P\mathbf{I}$ with \mathbf{I} being an identity tensor. Then Eq.(1) becomes

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

Since $d\mathbf{h}$ is now the conjugate variable of the force $-P\sigma_{\mathbf{h}}$ acting on the cell surface $\sigma_{\mathbf{h}}$, in view of the above principle of statistical physics, we have

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

Eq.(4) has the same form on the right side as that in Eq.(2), except the plus/minus sign. However, this equation is for crystals under external pressure, while Eq.(2) is for external stress, as shown on the left sides.

Since the cell volume $V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$, it follows

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

Then Eq.(3) can be rewritten as in the widely-used way

$$dW = -PdV. \quad (6)$$

As the cell volume V is the conjugate variable of the pressure P , based on the principle of statistical physics again, we have

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}. \quad (7)$$

This equation is shown in many many publications, for instance, as in Equation (2.96) from the statistical reference book[2]. It 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, Eq.(7) is not about the period vectors explicitly. Combining Eq.(7) and Eq.(4) would be very interesting:

$$\begin{aligned} PV &= \frac{V}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{\mathbf{a}}{\beta} \cdot \frac{\partial \ln Z}{\partial \mathbf{a}} \\ &= \frac{\mathbf{b}}{\beta} \cdot \frac{\partial \ln Z}{\partial \mathbf{b}} = \frac{\mathbf{c}}{\beta} \cdot \frac{\partial \ln Z}{\partial \mathbf{c}}. \end{aligned} \quad (8)$$

This means that the cell shape must keep certain symmetries for external pressure. Under such circumstances, Eq.(4) for any specific period vector, e.g. $\mathbf{h} = \mathbf{b}$, should be equivalent to Eq.(7). However, since neither Eq.(4) nor Eq.(7) applies, there is no similar cell shape restriction as shown in Eq.(8), on crystals under general external stress.

Then, as expected, Eq.(1) reduces to Eq.(3) and further to Eq.(6), whereas Eq.(2) reduces to Eq.(4) and further to Eq.(7) for the situation of external pressure.

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

$$\mathbf{P}^{(\text{int})} = \frac{1}{\beta V} \sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}} \frac{\partial \ln Z}{\partial \mathbf{h}} \otimes \mathbf{h}. \quad (9)$$

Let us do three right dot products on Eq.(9) 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

$$\mathbf{P}^{(\text{int})} \cdot \sigma_{\mathbf{h}} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \quad (10)$$

Bringing Eq.(10) into Eq.(2), then

$$\Upsilon \cdot \sigma_{\mathbf{h}} = -\mathbf{P}^{(\text{int})} \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (11)$$

which is equivalent to

$$\Upsilon + \mathbf{P}^{(\text{int})} = 0, \quad (12)$$

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

Since Eq.(12) means that the internal and the external stresses balance each other, Eq.(2) is actually the mechanical equilibrium condition for crystals under external stress and temperature, with the aid of the internal stress expressed by Eq.(9). If Eq.(2) cannot be satisfied, the system cannot exist. For example, if the temperature is increased to such a point that Eq.(2) cannot hold, it should be the melting temperature. Here it also shows that Eq.(2) and the internal stress expression are consistent with each other.

V. EQUATION OF STATE AND SYSTEM EXPANSION

In fact, Eq.(2) 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.(2) must be combined with Newton’s second law or the Schrödinger equation for motions of all particles in the cell. Since all particle motions can be solved by Newton’s second law and/or the Schrödinger equation, for a given set of the period vectors as parameters, Eq.(2) can be used to solve the period vectors for given external stress, temperature, and the solved particle motions. This procedure should be repeated until all variables converge. Since Newton’s second law and the Schrödinger 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.(2) for external conditions. Then Eq.(2) 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.(2) under all relevant external conditions. Alternatively, for example, supposing the temperature is fixed but the external stress is changed, one can do partial derivatives of Eq.(2) with respect to the changed components of the external stress, then get 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.(2), $-kT\partial \ln Z(\omega, T)/\partial \mathbf{h}$, should change. Then the left side of Eq.(2), $\Upsilon \cdot \sigma_{\mathbf{h}}$, should also change. Since the external stress Υ 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 so with respect to the cell. 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. Specifically, the directions of the period vectors can be set fixed, and their lengths can be set proportional to $V^{1/3}$. Furthermore, all particle (equilibrium) position vectors should be functions of the period vectors, also meaning functions of V . Then Eq.(2) is only about the crystal cell volume, the external pressure, and the temperature variables, a pure traditional form of the equation of state.

VI. WORK AND ENERGY IN QUASI-EQUILIBRIUM PROCESS

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 process, the system should be in an instantaneous equilibrium state, satisfying Eq.(2), then the whole process 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.(1) from the initial state to the final state, we get the work done by the external stress for the whole process:

$$W = \int_{\mathbf{a}_i}^{\mathbf{a}_f} (\mathbf{\Upsilon} \cdot \sigma_{\mathbf{a}}) \cdot d\mathbf{a} + \int_{\mathbf{b}_i}^{\mathbf{b}_f} (\mathbf{\Upsilon} \cdot \sigma_{\mathbf{b}}) \cdot d\mathbf{b} + \int_{\mathbf{c}_i}^{\mathbf{c}_f} (\mathbf{\Upsilon} \cdot \sigma_{\mathbf{c}}) \cdot d\mathbf{c}. \quad (13)$$

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 process can be expressed as

$$Q = E_{t,f} - E_{t,i} - W. \quad (14)$$

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.(2), the equation of state, the period vectors should also be changed, then to employ Eq.(2) to calculate the changed crystal structure accurately would be very helpful in these studies.

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

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

First of all, the 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. In any case, let us suppose the elasticity theory also studies microscopic structures of crystals in the following.

Second, the 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 $\mathbf{r}_{i,0}$ ($i = 1, \dots, N$) in the center cell should be supposed known, where N is the total number of particles in the cell. This work only focuses on the current state under certain external stress, forgetting all other states completely. In other words, this work studies any individual state completely independently, with no information from any other state needed.

Third, the 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:

$$\mathbf{h} = \mathbf{h}_0 + \mathbf{u} \cdot \mathbf{h}_0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (15)$$

$$\mathbf{r}_i = \mathbf{r}_{i,0} + \mathbf{u} \cdot \mathbf{r}_{i,0} \quad (i = 1, \dots, N), \quad (16)$$

as well. Since Eqs.(15) and (16) 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.(15) and (16), but regards and uses all the period vectors ($\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}$) and the particle position vectors \mathbf{r}_i ($i = 1, \dots, N$) as completely independent variables with each other. Then this work 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 Schrödinger equation, this work only focuses on how to determine the period vectors.

Furthermore, the 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.(2) is the temperature-dependent relationship between them, but with no additional constants or coefficients introduced, supposing everything in Eq.(2) can be at least calculated numerically. Then Eq.(2) 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.(2) under a series of values of the external stress, for a given temperature.

C. Consistency with the previous work 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

$$Z = Z_k Z_u, \quad (17)$$

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

$$Z_k = \frac{V^N}{N!} \int \int \dots \int \frac{1}{h^{3N}} e^{-\beta E_k(\mathbf{p})} d\mathbf{p}, \quad (18)$$

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

$$Z_u = \frac{1}{V^N} \int_V \int_V \dots \int_V e^{-\beta E_p(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{R})} d\mathbf{R}, \quad (19)$$

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

Since the integration in Eq.(18) has nothing to do with the period vectors, the derivative

$$\frac{\partial \ln Z_k}{\partial \mathbf{h}} = \frac{N}{V} \frac{\partial V}{\partial \mathbf{h}} = \frac{N}{V} \sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \quad (20)$$

But a little more patience is needed for Eq.(19), as 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:

$$\mathbf{r}_i = r_{i,\mathbf{a}}\mathbf{a} + r_{i,\mathbf{b}}\mathbf{b} + r_{i,\mathbf{c}}\mathbf{c} \quad (i = 1, \dots, N), \quad (21)$$

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

$$r_{i,\mathbf{h}} = \frac{1}{V} \mathbf{r}_i \cdot \sigma_{\mathbf{h}} \quad (i = 1, \dots, N; \mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \quad (22)$$

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

$$\begin{aligned} \frac{1}{V} \int_V \dots d\mathbf{r}_i &= \int_V \dots \frac{d\mathbf{r}_i}{V} \\ &= \int_0^1 \int_0^1 \int_0^1 \dots dr_{i,\mathbf{a}} dr_{i,\mathbf{b}} dr_{i,\mathbf{c}} \\ &\quad (i = 1, \dots, N). \end{aligned} \quad (23)$$

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:

$$\begin{aligned} \frac{\partial Z_u}{\partial \mathbf{h}} &= \int_0^1 \int_0^1 \int_0^1 \int_0^1 \int_0^1 \int_0^1 \dots \int_0^1 \int_0^1 \int_0^1 \times \\ &\quad \frac{\partial}{\partial \mathbf{h}} e^{-\beta E_p(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{R})} dr_{1,\mathbf{a}} dr_{1,\mathbf{b}} dr_{1,\mathbf{c}} \times \\ &\quad dr_{2,\mathbf{a}} dr_{2,\mathbf{b}} dr_{2,\mathbf{c}} \dots dr_{N,\mathbf{a}} dr_{N,\mathbf{b}} dr_{N,\mathbf{c}} \\ &\quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \end{aligned} \quad (24)$$

Since that the dependency of \mathbf{R} on the period vectors must be considered as in Eq.(21) now, the following derivatives should be separated as

$$\frac{\partial E_p}{\partial \mathbf{h}} = \frac{\partial E_p(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{R})}{\partial \mathbf{h}} \Big|_{\mathbf{R}} + \frac{\partial E_p(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{R})}{\partial \mathbf{h}} \Big|_{\mathbf{a}, \mathbf{b}, \mathbf{c}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (25)$$

where

$$\begin{aligned} \frac{\partial E_p(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{R})}{\partial \mathbf{h}} \Big|_{\mathbf{a}, \mathbf{b}, \mathbf{c}} &= \sum_{i=1}^N \frac{\partial E_p(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{R})}{\partial \mathbf{r}_i} \frac{\partial \mathbf{r}_i}{\partial \mathbf{h}} \\ &= \sum_{i=1}^N -\mathbf{F}_i r_{i,\mathbf{h}} \\ &= \sum_{i=1}^N -\mathbf{F}_i \frac{\mathbf{r}_i \cdot \sigma_{\mathbf{h}}}{V} \\ &= -\frac{1}{V} \sum_{i=1}^N (\mathbf{F}_i \otimes \mathbf{r}_i) \cdot \sigma_{\mathbf{h}} \\ &\quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \end{aligned} \quad (26)$$

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.(24, 25, and 26), it follows

$$\begin{aligned} -\frac{\partial \ln Z_u}{\beta \partial \mathbf{h}} &= -\frac{1}{\beta Z_u} \frac{\partial Z_u}{\partial \mathbf{h}} \\ &= \frac{-kT}{Z_u V^N} \int_V \int_V \dots \int_V \frac{\partial}{\partial \mathbf{h}} e^{-\beta E_p(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{R})} d\mathbf{R} \\ &= \frac{1}{Z_u V^N} \int_V \int_V \dots \int_V e^{-\beta E_p(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{R})} \times \\ &\quad \left(\frac{\partial E_p(\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{R})}{\partial \mathbf{h}} \Big|_{\mathbf{R}} - \frac{1}{V} \sum_{i=1}^N \mathbf{F}_i \otimes \mathbf{r}_i \cdot \sigma_{\mathbf{h}} \right) d\mathbf{R} \\ &\quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \end{aligned} \quad (27)$$

Bringing Eqs.(20) and (27) into Eq.(2), we get

$$\Upsilon \cdot \sigma_{\mathbf{h}} = -\frac{1}{V} NkT \sigma_{\mathbf{h}} - \frac{1}{\beta} \frac{\partial \ln Z_u}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \quad (28)$$

For "crystals" only containing ideal gases under external pressure, Eq.(28) becomes the ideal gas law: $PV = NkT$.

Now let us consider equilibrium states where

$$\ddot{\mathbf{h}} = 0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (29)$$

$$\ddot{\mathbf{r}}_i = 0 \quad (i = 1, \dots, N). \quad (30)$$

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

$$\begin{aligned} \Upsilon \cdot \sigma_{\mathbf{h}} &= -\frac{2}{3V} \sum_{i=1}^N \frac{1}{2} m_i |\dot{\mathbf{r}}_i|^2 \sigma_{\mathbf{h}} + \\ &\quad + \frac{\partial E_p}{\partial \mathbf{h}} \Big|_{\mathbf{R}} - \frac{1}{V} \sum_{i=1}^N (\mathbf{F}_i \otimes \mathbf{r}_i) \cdot \sigma_{\mathbf{h}} \\ &\quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \end{aligned} \quad (31)$$

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.(28) as shown in Eq.(27) 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.(31), 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.(28) achieved in statistical physics here and Eq.(31) previously derived based on the Newtonian dynamics[1] are consistent with 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 Eq.(9), then get

$$\alpha_{\mathbf{h},\mathbf{h}} \ddot{\mathbf{h}} = (\boldsymbol{\Upsilon} + \mathbf{P}^{(\text{int})}) \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (32)$$

where $\alpha_{\mathbf{h},\mathbf{h}}$ is an equivalent mass, then can be chosen with any positive real number. Eq.(32) can be used as an “algorithm” for solving Eq.(2) in both classical physics and quantum physics. It tells us in which directions the period vectors should be increased if the internal and the external stresses do not balance each other.

In the Born-Oppenheimer approximation, ions and electrons in crystals are usually solved by the Newtonian dynamics and quantum mechanics separately. Then the partition function of the whole system can be factorized accordingly, then Eq.(2) is the combination of classical physics and quantum physics.

VIII. A ONE-DIMENSIONAL SIMPLIFIED MODEL SYSTEM

In 2010, Ma and Tuckerman applied Eq.(2) (Equations (1) and (2) in their paper) 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. 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 pulling force. If $f_{ext} < 0$, it presses the system inwards, then is a pressing 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

$$E_k = \frac{3}{2} kT. \quad (33)$$

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

$$\varphi^{(L-J)}(r) = 4\epsilon \left[\left(\frac{\lambda}{r} \right)^{12} - \left(\frac{\lambda}{r} \right)^6 \right], \quad (34)$$

where r is the distance between the atoms, $\epsilon = 3.500 \times 10^{-20} \text{J}$, and $\lambda = 2.800 \text{\AA}$. Then the force on an atom at r by the atom at the origin is

$$\begin{aligned} f^{(L-J)}(r) &= -\frac{d}{dr} \varphi^{(L-J)}(r) \\ &= \frac{4\epsilon}{r} \left[12 \left(\frac{\lambda}{r} \right)^{12} - 6 \left(\frac{\lambda}{r} \right)^6 \right]. \end{aligned} \quad (35)$$

Based on Eq.(34), 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:

$$\begin{aligned} E_p^{(L-J)}(a) &= \frac{1}{2} \sum_{j=-\infty}^{\infty (j \neq 0)} \varphi^{(L-J)}(ja) \\ &= \sum_{j=1}^{\infty} 4\epsilon \left[\left(\frac{\lambda}{ja} \right)^{12} - \left(\frac{\lambda}{ja} \right)^6 \right]. \end{aligned} \quad (36)$$

Then the total energy of the center cell is

$$E_t = E_k + E_p^{(L-J)}(a). \quad (37)$$

Bringing Eqs.(33) and (36) into Eq.(31), we get the equation for the period:

$$f_{ext} + \frac{kT}{a} + F_{L \rightarrow R}(a) = 0, \quad (38)$$

where

$$\begin{aligned} F_{L \rightarrow R}(a) &= -\frac{d}{da} E_p^{(L-J)}(a) \\ &= \frac{1}{2} \sum_{j=-\infty}^{\infty (j \neq 0)} j f^{(L-J)}(ja) \\ &= \sum_{j=1}^{\infty} j f^{(L-J)}(ja) \\ &= \sum_{j=1}^{\infty} \frac{4\epsilon}{a} \left[12 \left(\frac{\lambda}{ja} \right)^{12} - 6 \left(\frac{\lambda}{ja} \right)^6 \right], \end{aligned} \quad (39)$$

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.(35) with the red line, and the net force $F_{L \rightarrow R}(a)$ via the system period a , as in Eq.(39), 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 term of the force $F_{L \rightarrow R}(a)$, as shown in Eq.(39). Since the two lines are almost completely coincident, the rest terms in Eq.(39) decrease very rapidly.

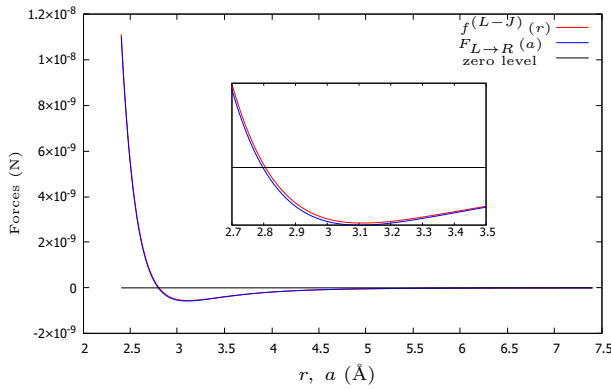


FIG. 2: The red line is the force on any atom by the atom in the center cell, as shown in Eq.(35); the blue line is the net force on the right half of the system by the left half when the system is bisected, as given in Eq.(39). As the data are very close, the two lines are almost completely coincident. The inside figure is an amplified one around the minimum forces.

FIG. 2 also shows that there is a minimum value in the force $F_{L \rightarrow R}(a)$. By taking derivative of this force with respect to the period, setting it as zero, and solving the equation

$$\begin{aligned} & \frac{d}{da} F_{L \rightarrow R}(a) \\ &= \sum_{j=1}^{\infty} -\frac{4\epsilon}{a^2} \left[12 \times 13 \left(\frac{\lambda}{ja} \right)^{12} - 6 \times 7 \left(\frac{\lambda}{ja} \right)^6 \right] \\ &= 0, \end{aligned} \quad (40)$$

we get the value:

$$a_{min} = \lambda \left(\frac{\sum_{j=1}^{\infty} 12 \times 13 j^{-12}}{\sum_{j=1}^{\infty} 6 \times 7 j^{-6}} \right)^{\frac{1}{6}} = 3.102 \text{Å}. \quad (41)$$

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

Still in FIG. 2, when the period a runs from zero to a_{min} , the force $F_{L \rightarrow R}(a)$ decreases monotonically, and when the period a runs from a_{min} to the positive infinity, the force $F_{L \rightarrow R}(a)$ 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 $F_{L \rightarrow R} < 0$, Eq.(38) becomes

$$f_{ext} = -F_{L \rightarrow R} > 0, \quad (42)$$

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 $f_{ext} > |F_{L \rightarrow R}|$ (even just a little bit), the atoms should move apart, and the period increases (this can also be observed based on Eq.(32)). Then $|F_{L \rightarrow R}|$ decreases, causing an actual imbalance between f_{ext} and $|F_{L \rightarrow R}|$. This causes atoms to move further apart, meaning the period becomes larger. The value $|F_{L \rightarrow R}|$ decreases more, causing more imbalance between f_{ext} and $|F_{L \rightarrow R}|$, meaning atoms move farther apart, until the system is broken. If the fluctuation factor results in $f_{ext} < |F_{L \rightarrow R}|$, a similar event will happen, however rather than breaking the system, the period becomes smaller and smaller, leaving the region $[a_{min}, \infty)$. Then an appropriate position in the region $(0, a_{min}]$ sets up a new equilibrium state. As for non-zero temperature, as the term kT/a is always positive as in Eq.(38), it can not make the system to become more stable in the region $[a_{min}, \infty)$. Then let us restrict all later calculation to the region $(0, a_{min}]$ regarding the period.

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

B. Constant external temperature

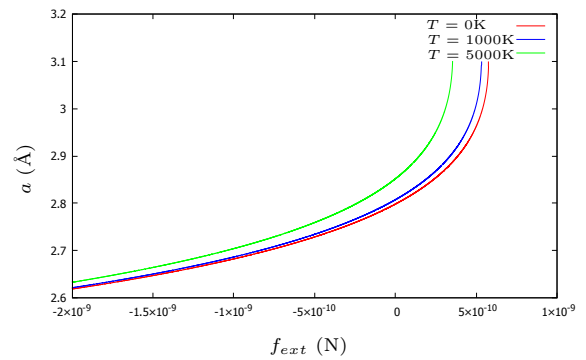


FIG. 3: Under constant temperatures at 0K, 1000K and 5000K respectively, the changing external force causes the system period changes.

FIG. 3 shows the changing system period by the changing external force, for three constant external temperatures. While the pressing force can take any negative value, since the force $F_{L \rightarrow R}(a)$ has the unique minimum value at a_{min} , the pulling force is actually limited to its

maximum based on Eq.(38)

$$\begin{aligned} f_{ext,max,pull} &= -F_{L \rightarrow R}(a_{min}) - \frac{kT}{a_{min}} \\ &= 5.769 \times 10^{-10} \text{N} \\ &\quad - (4.452 \times 10^{-14} \text{N K}^{-1}) T. \end{aligned} \quad (43)$$

Otherwise, the system will be pulled broken.

For the external force ranging from zero to $f_{ext,e} = 1.0 \times 10^{-10} \text{N}$, suppose that the period and the external force change approximately linearly. The elastic constants of the Hooke's law, τ , can be calculated as in TABLE I, where a_0 and a_1 are the periods corresponding to the zero external force and $f_{ext,e}$ respectively, and $\Delta f_{ext} = f_{ext,e} - 0 = 1.0 \times 10^{-10} \text{N}$ is the change of the external force.

TABLE I: Elastic constants of the Hooke's law: τ

$T(\text{K})$	$a_0(\text{\AA})$	$(a_1 - a_0)(\text{\AA})$	$\tau = \frac{\Delta f_{ext}}{(a_1 - a_0)/a_0} (\text{N})$
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}

Then the Hooke's law can be expressed as

$$f_{ext} \approx \tau \frac{a - a_0}{a_0}. \quad (44)$$

In fact, the changing relationship between the period and the external force can also be calculated by taking the derivative of Eq.(38) with respect to the period.

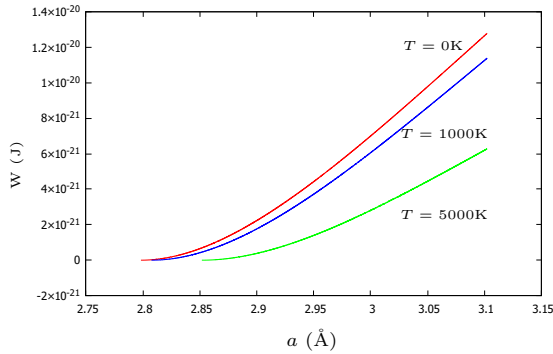


FIG. 4: Under three constant temperatures respectively, the work done by the external force in the quasi-equilibrium process from the state of zero external force to the state of a_{min} .

Employing Eq.(13) 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 process under the three constant temperatures can be calculated and shown in FIG. 4. Through Eq.(14) and (37), the heat absorbed by the system during this process is shown in FIG. 5.

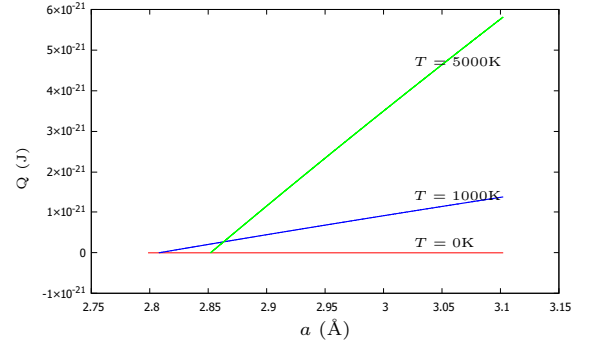


FIG. 5: Under the three constant temperatures respectively, the heat absorbed by the system in the quasi-equilibrium process from the state of zero external force to the state of a_{min} .

For zero temperature, FIG. 5 shows that no heat is needed by the system from outside. Imagine that an object is running in a potential field of $E_p^{(L-J)}(r)$, where r is its distance to the coordinate origin, as shown in Eq.(36). It should experience the force acted upon it by the field as $-dE_p^{(L-J)}(r)/dr$. According to the first line of Eq.(39), that force is exactly the force $F_{L \rightarrow R}(a)$ for $r = a$. Further considering the force balance relationship in Eq.(42), the quasi-equilibrium process in which the external force pulls the system period to increase is the same in physics as the process 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 process, the energy needed for the potential change is accurately compensated by the work done by the person who raised it, requiring no additional energy exchange. This is what happens for zero temperature in FIG. 5. For non-zero constant temperatures, the system kinetic energy as shown in Eq.(33) is also fixed, so there is no change of it between the initial and the final states, and no heat is needed from the kinetic energy perspective. Furthermore, Eq.(38) means that the difference between the external force and the force $F_{L \rightarrow R}(a)$ is kT/a . In FIG. 5, 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 by an external force of fixed difference from its weight, the additional energy needed to compensate the change in potential over the work done by the external force should be proportional to the change of the object's height/altitude. For the same reason, we see the lines in FIG. 5 are almost straight 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 contacting with the system surfaces, when their temperatures are different.

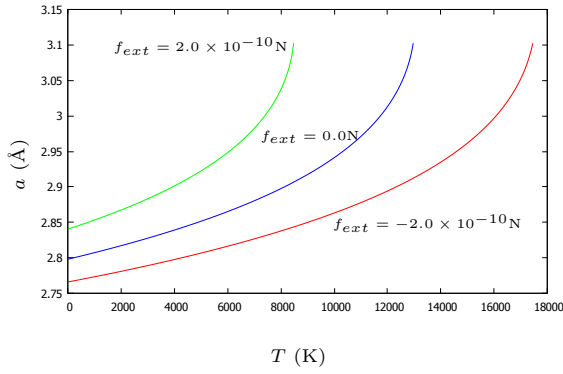


FIG. 6: Under three constant external forces respectively, the period is changed by the temperature.

C. Constant external force

FIG. 6 is the period changed by the temperature for three given external forces. Again based on Eq.(38), since the force $F_{L \rightarrow R}(a)$ has the unique minimum value at a_{min} , there is the upper limit

$$\begin{aligned} T_{max} &= -\frac{a_{min}}{k} (f_{ext} + F_{L \rightarrow R}(a_{min})) \\ &= -2.247 \times 10^{13} \text{K N}^{-1} (f_{ext} - 5.769 \times 10^{-10} \text{N}), \end{aligned} \quad (45)$$

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 pulling force or the stronger pressing force, the higher melting point.

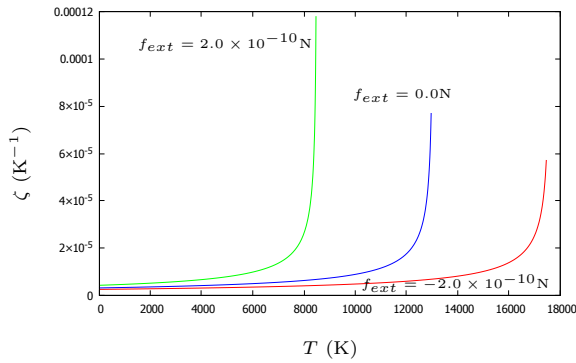


FIG. 7: The relative coefficient of thermal expansion with temperature under the three given external forces.

If we take the derivative of Eq.(38) with respect to the period a under the constant external force, then get the relative coefficient of thermal expansion as

$$\zeta = \frac{1}{a} \frac{da}{dT} = \frac{k}{a^2} \left(\frac{kT}{a^2} - \frac{d}{da} F_{L \rightarrow R}(a) \right)^{-1}, \quad (46)$$

which is shown in FIG. 7 for the three given external forces. Since as shown in FIG. 2, the force $F_{L \rightarrow R}(a)$ 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 $F_{L \rightarrow R}(a)$ plays in Eq.(38), FIG. 7 presents the top values of the relative coefficient of thermal expansion, 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 process 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. For this example, the FORTRAN 90 source code can be obtained by sending emails to the author.

IX. SUMMARY

Eq.(2) was derived for determining crystal period vectors, then predicting crystal structures, by formulating the work done by the external stress on the crystal and the application of the statistical physics principles. The existing statistical theory for the external pressure was covered as a special case. While the previously derived equation for the period vectors in the framework of the Newtonian dynamics can be combined with quantum mechanics, Eq.(2) applies to both classical physics and quantum physics by itself. While consistent with each other in classical physics, they can be combined.

It also turned out that Eq.(2) is not only the mechanical 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.(2) is also the microscopic but temperature-dependent form of the generalized Hooke's law, for linear elastic crystals, and can be used to calculate the corresponding elastic constants for given temperatures. It should play an essential role in piezoelectric and piezomagnetic studies, caused by an increase of the external pressure on crystals only in one direction, as well. In conclusion, the maximum external pulling force before the system is broken, melting temperature, period changed by the external force and temperature, Hooke's law, and thermodynamic properties and processes were demonstrated in a one-dimensional simplified model.

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 - [4] Z. Ma, M. Tuckerman, *J. Chem. Phys.* **133**, 184110 (2010). <https://doi.org/10.1063/1.3499812> .
 - [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 $A_i = -kT \partial \ln Z / \partial B_i$. It is shown as in Equations (2.95), (3.3), and (3.129) of the statistical reference book[2].