

Microscopic Equations of State, Thermodynamical Properties, and System Collapse: Application of the Dynamical Equation of Period Vectors in Crystal Structure Prediction under External Temperature and Stress/Pressure (Version 2.1)

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In crystal structure prediction, Newton's second law can always be applied to particles (atoms or ions) in a cell to determine their positions. However the values of the period vectors (crystal cell edge vectors) should be determined as well. Here we applied the dynamical equation of period vectors derived recently based on Newton's laws (doi:/10.1139/cjp-2014-0518) for that purpose, where the period vectors are driven by the imbalance between the internal and external pressures/stresses. Since the internal stress has both a full kinetic energy term and a full interaction term, the influences of both external temperature and stress/pressure on crystal structures can be calculated, then thermodynamical properties and processes were presented. Contrary to usual ideas, the equations show that pure harmonic vibrating phonons can result in thermal expansion in crystals when the external temperature is changed. Finally, crystal system collapse due to temperature and/or stress/pressure change was discussed.

I. INTRODUCTION

Crystal structure prediction from being questioned becomes more and more feasible and important these years[1–6]. Actually minimizing the enthalpy $H = E + PV$ is normally employed to determine crystal structures for constant external pressure P , where E and V are the total potential energy and volume of a crystal cell respectively. Then, one has

$$\frac{\partial(E + PV)}{\partial \mathbf{r}_i} = 0 \quad (i = 1, 2, \dots, n), \quad (1)$$

$$\frac{\partial(E + PV)}{\partial \mathbf{h}} = 0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (2)$$

where n is the total number of particles (atoms or ions) in a cell, \mathbf{r}_i is the position vector of particle i , and \mathbf{h} is any one of the period vectors (cell edge vectors) \mathbf{a} , \mathbf{b} , and \mathbf{c} . Eq.(1) means

$$\mathbf{F}_i = -\frac{\partial E}{\partial \mathbf{r}_i} = 0 \quad (i = 1, 2, \dots, n), \quad (3)$$

where \mathbf{F}_i is the net force acting on particle i . Eq.(2) means

$$\frac{\partial E}{\partial \mathbf{h}} + P\sigma_h = 0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (4)$$

where $\sigma_h = \partial V / \partial \mathbf{h}$ is the cell surface vector with respect to \mathbf{h} . Actually the way in our previous paper[7] is equivalent to this. However the temperature effect is not shown there.

Another way making much progress in crystal structure prediction is minimizing Gibbs free energy and applying quasiharmonic Debye model[8–14] for phonon (then temperature) effect[15–19]. However, they usually use the cell volume as variable rather than the period vectors. Additionally all above only consider the external pressure, rather than the general external stress.

In this paper, we will apply the dynamical equation of period vectors derived recently[20] in crystal structure prediction, with temperature including phonon effect applied, and external stress considered.

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II. DYNAMICAL EQUATION OF PERIOD VECTORS IN CRYSTAL STRUCTURE PREDICTION

In our recent paper[20], particles are always obeying Newton's second law

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i \quad (i = 1, 2, \dots, n). \quad (5)$$

When the system reaches an equilibrium state, Eq.(5) becomes Eq.(3). For determining the period vectors, the dynamical equation of them were derived based on Newton's laws as[20]

$$\alpha_{\mathbf{h},\mathbf{h}} \ddot{\mathbf{h}} = (\pi + \Upsilon) \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (6)$$

where $\alpha_{\mathbf{h},\mathbf{h}}$ is some mass, tensor π is the internal stress, and tensor Υ is the external stress. As a matter of fact, crystal structure normally means the values of particle position vectors and the period vectors in an equilibrium state, then let us regard all the so-called degrees of freedom (DOF) of the system in the paper[20], which are $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \mathbf{a}, \mathbf{b}$, and \mathbf{c} , as those in the equilibrium state. Since the purpose of pursuing a crystal structure is to determine their final values from some guessed ones, the velocities of them can be completely forgotten. Then let us ignore the left side of Eq.(6), but only change the period vectors in the directions of the calculated result of the right side of Eq.(6).

The internal stress in Eq.(6) has two terms

$$\pi = \tau + \varepsilon. \quad (7)$$

The first term

$$\tau = \frac{1}{3V} \sum_{i=1}^n m_i |\dot{\mathbf{r}}_i|^2 \mathbf{I} = \frac{2}{3V} E_{k,MD} \mathbf{I}, \quad (8)$$

where $E_{k,MD}$ is the total kinetic energy of the particles in the center cell and \mathbf{I} is an identity tensor, then this term should be temperature dependent. Although no kinetic energy for the DOF variables, which are the crystal framework (backbone) in equilibrium states, other kinetic energy do exist in the system separately. For example, the actual position vector of particle i is $\mathbf{r}_i + \Delta \mathbf{r}_{i,vb} + \Delta \mathbf{r}_{i,th}$, where as we already know \mathbf{r}_i is the equilibrium one, $\Delta \mathbf{r}_{i,vb}$ is vibrational displacement around and relative to the equilibrium, and $\Delta \mathbf{r}_{i,th}$ is thermal displacement around and relative to the vibration. In other words, it performs three motions at the same time: equilibrium position motion (static once achieved), ordered vibration, and disordered thermal motion. Then the kinetic energy of the particles can be separated into two additive terms of ordered motion and disordered thermal motion respectively, and the ordered kinetic energy can be further separated into two additive ones of the DOF variables (but zero here) and of the vibration. Additionally kinetic energy of free electrons should also be considered, which are also "particles", while potential energy associated with electrons is always included in the total potential energy in any form. Then Eq.(8) can be further written as

$$\tau = \tau_{vb} + \tau_{th} + \tau_{el}, \quad (9)$$

where τ_{el} , τ_{th} , and τ_{vb} are contributed from the kinetic energies of free electron's motion, (other) particle's thermal motion (disordered), and particle's vibrations (ordered) respectively. Specifically,

$$\tau_{vb} = \frac{2}{3V} E_{k,MD,vb} \mathbf{I}, \quad (10)$$

$$\tau_{el} = \frac{2}{3V} E_{k,MD,el} \mathbf{I}, \quad (11)$$

where $E_{k,MD,vb}$ and $E_{k,MD,el}$ are the kinetic energies of the particle's vibrations and free electron's motion per cell. For the particle's thermal motion, it could be written as

$$\tau_{th} = \frac{1}{V} nkT \mathbf{I}, \quad (12)$$

where k is Boltzmann constant and T is the temperature. However any of these tensor items may be ignored if the corresponding actual physics process is negligible.

The second term of the internal stress is

$$\varepsilon = -\frac{1}{V} \sum_{\mathbf{z} \in \text{DOF}} \left(\frac{\partial E_{p,MD}}{\partial \mathbf{z}} \right) \otimes \mathbf{z}, \quad (13)$$

where $E_{p,MD}$, a function of the DOF, is the total potential energy of a cell, which should be the same as E in Eq.(1). Explicitly, it is

$$\varepsilon = \frac{1}{V} \left(\sum_{i=1}^n \mathbf{F}_i \otimes \mathbf{r}_i - \frac{\partial E}{\partial \mathbf{a}} \otimes \mathbf{a} - \frac{\partial E}{\partial \mathbf{b}} \otimes \mathbf{b} - \frac{\partial E}{\partial \mathbf{c}} \otimes \mathbf{c} \right). \quad (14)$$

Considering Eq.(3) (equilibrium states), it becomes

$$\varepsilon = -\frac{1}{V} \left(\frac{\partial E}{\partial \mathbf{a}} \otimes \mathbf{a} + \frac{\partial E}{\partial \mathbf{b}} \otimes \mathbf{b} + \frac{\partial E}{\partial \mathbf{c}} \otimes \mathbf{c} \right). \quad (15)$$

Since in equilibrium states $\ddot{\mathbf{h}} = 0$ and using $\mathbf{h}' \cdot \sigma_h = \delta_{\mathbf{h},\mathbf{h}'} V$, where $\mathbf{h}' = \mathbf{a}$ or \mathbf{b} or \mathbf{c} , Eq.(6) is

$$\tau \cdot \sigma_h - \frac{\partial E}{\partial \mathbf{h}} + \Upsilon \cdot \sigma_h = 0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \quad (16)$$

Recalling the derivation of Eq.(6) in our paper[20], Eq.(16) actually means that if the crystal is imagined being cut into two halves, the net of all forces on each half is zero. Then the combination of Eq.(3) and Eq.(16) determine the crystal structure for given external temperature and stress. For equilibrium states, the internal temperature should be the same as the external temperature. As the period vectors determine the cell volume, they are actually also equations of state of crystals, but in a microscopic form.

III. UNDER EXTERNAL PRESSURE

For the special case of external pressure P , $\Upsilon = -P\mathbf{I}$ (real number P should be positive for compressing and negative for stretching), after being multiplied with period vector \mathbf{h} , Eq.(16) reduces to

$$nkT + \frac{2}{3}E_{k,MD,el} + \frac{2}{3}E_{k,MD,vb} - L - PV = 0, \quad (17)$$

where

$$L = \left(\frac{\partial E}{\partial \mathbf{a}} \right) \cdot \mathbf{a} = \left(\frac{\partial E}{\partial \mathbf{b}} \right) \cdot \mathbf{b} = \left(\frac{\partial E}{\partial \mathbf{c}} \right) \cdot \mathbf{c}. \quad (18)$$

Comparing Eq.(4) and Eq.(17), we have extra kinetic energy terms reflecting the influence of temperature on crystal structures. For equilibrium states under external pressure, Eq.(17) also allows us to specify the internal pressure as

$$P_{int} = \frac{2}{3V}E_{k,MD} - \frac{L}{V}. \quad (19)$$

IV. THERMODYNAMICS

Since crystal structures can be determined based on the microscopic equations of state (Eq.(3) and Eq.(16)), let us explore their thermodynamical properties and processes in the following three cases.

A. Isovolumic

Now let us consider the temperature is changed from T to T' but keep the volume fixed. Actually, the fixed volume means the crystal structure does not change, then Eq.(3) is always satisfied, and the total potential energy is also fixed. However, in order to satisfy Eq.(16), since $\partial E/\partial \mathbf{h}$ does not change, the externally applied stress must change accordingly from Υ to Υ' as the temperature dependent (kinetic energy) part of the internal stress changes from τ to τ'

$$\Upsilon' = \Upsilon + \tau - \tau'. \quad (20)$$

The heat capacity at constant volume is then

$$C_V = \left(\frac{dE_{k,MD}}{dT} \right)_V. \quad (21)$$

B. Isobaric

When the temperature is changed from T to T' , even with the external stress Υ kept fixed, the crystal structure must change accordingly in order to satisfy Eq.(3) and Eq.(16). As a result, the volume should change from V to V' , for an example. Then the coefficient of isobaric thermal expansion can be quickly calculated as

$$\zeta = \frac{1}{V} \left(\frac{dV}{dT} \right)_{\Upsilon} \approx \frac{1}{V} \frac{V' - V}{T' - T}. \quad (22)$$

The heat capacity at constant external pressure

$$C_P = \left(\frac{d(E_{k,MD} + E_{p,MD})}{dT} + P \frac{dV}{dT} \right)_P \quad (23)$$

can also be calculated the same way.

An alternative more accurate way to calculate them is to take derivatives of Eq.(3) and Eq.(16) with respect to temperature, since the equations should always be satisfied even if the external conditions are changed:

$$\frac{d\mathbf{F}_i}{dT} = 0 \quad (i = 1, 2, \dots, n), \quad (24)$$

$$\frac{d}{dT} \left\{ \tau \cdot \sigma_h - \frac{\partial E}{\partial \mathbf{h}} + \Upsilon \cdot \sigma_h \right\} = 0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \quad (25)$$

Please note that all these are vector equations, then they are total $3(n+3)$ scalar equations. In Cardesian coordinates, for every coordinate component $k = x, y, z$, the component $F_{i,k}$ of the force \mathbf{F}_i is a function of DOF, then

$$\frac{dF_{i,k}}{dT} = \sum_{\mathbf{z} \in \text{DOF}} \frac{\partial F_{i,k}}{\partial \mathbf{z}} \cdot \frac{d\mathbf{z}}{dT} = 0 \quad (i = 1, 2, \dots, n), (k = x, y, z). \quad (26)$$

As all the partial derivatives $\partial F_{i,k}/\partial \mathbf{z}$ are supposed known, all these total $3n$ equations are linear ones about the derivatives of DOF with respect to temperature ($d\mathbf{r}_1/dT$, $d\mathbf{r}_2/dT$, \dots , $d\mathbf{r}_n/dT$, $d\mathbf{a}/dT$, $d\mathbf{b}/dT$, and $d\mathbf{c}/dT$).

Very similarly,

$$-\frac{d}{dT} \frac{\partial E}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}) \quad (27)$$

are all linear combinations of the derivatives of DOF with respect to temperature. For example, $\mathbf{h} = \mathbf{a}$, considering constant stress Υ , then

$$\frac{d}{dT} (\Upsilon \cdot \sigma_a) = \Upsilon \cdot \frac{d\sigma_a}{dT} = \Upsilon \cdot \left(\frac{d\mathbf{b}}{dT} \times \mathbf{c} + \mathbf{b} \times \frac{d\mathbf{c}}{dT} \right), \quad (28)$$

also a linear combination of the derivatives of DOF with respect to temperature. Assuming $d(\tau \cdot \sigma_h)/dT$ can also be expanded as a linear combination of the derivatives of DOF with respect to temperature, we will get a system of $3(n+3)$ linear equations about the derivatives of DOF with respect to temperature. Once solved, the coefficients of isobaric thermal expansion can be calculated as

$$\zeta = \frac{1}{V} \left(\frac{dV}{dT} \right)_{\Upsilon} = \sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}} \frac{\sigma_h}{V} \cdot \frac{d\mathbf{h}}{dT}. \quad (29)$$

The heat capacity at constant external pressure can be calculated the same way.

If the system expansion is assumed/proven evenly to certain degrees, the number of independent equations of the linear system should be reduced significantly.

C. Isothermal

In this case, an external pressure, rather than a stress, is applied to the system. Everything is similar to the isobaric case, but the derivatives should be taken of Eq.(3) and Eq.(17) with respect to pressure:

$$\frac{d\mathbf{F}_i}{dP} = 0 \quad (i = 1, 2, \dots, n), \quad (30)$$

$$\frac{d}{dP} \left\{ \frac{2}{3} E_{k,MD,el} + \frac{2}{3} E_{k,MD,vb} - L - PV \right\} = 0. \quad (31)$$

Considering $dT/dP = 0$ for isothermal condition and supposing the above equations also generate a system of $3(n+3)$ linear equations but about the derivatives of DOF with respect to pressure, the coefficients of isothermal compressibility can be calculated as

$$\beta = -\frac{1}{V} \left(\frac{dV}{dP} \right)_T = - \sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}} \frac{\sigma_{\mathbf{h}}}{V} \cdot \frac{d\mathbf{h}}{dP}. \quad (32)$$

V. PHONON EFFECTS

Since many studies show that phonons play a very important role in crystal thermodynamical processes[8–14], let us consider phonons. Based on quantum statistics, the total energy of phonons of fixed frequency ω_j is [11, 15–19]

$$E_{t,j} = \frac{1}{2} \hbar \omega_j + \frac{\hbar \omega_j}{\exp(\hbar \omega_j / kT) - 1}, \quad (33)$$

where $\hbar = h/2\pi$ and h is Planck's constant. Then the total potential energy of phonons per cell is

$$E_{t,MD,vb} = \sum_{j=1}^{3n} E_{t,j}. \quad (34)$$

As a matter of fact, the kinetic energy and potential energy is averagely equal in harmonic vibrations, then the total kinetic energy of phonons per cell should be

$$E_{k,MD,vb} = \frac{1}{2} E_{t,MD,vb} = \frac{1}{2} \sum_{j=1}^{3n} \hbar \omega_j \left(\frac{1}{2} + \frac{1}{\exp(\hbar \omega_j / kT) - 1} \right). \quad (35)$$

The other half is the total potential energy of phonons per cell $E_{p,MD,vb} = \frac{1}{2} E_{t,MD,vb}$. Theoretically it should be included in E , the total potential energy of a cell, in Eq.(16). As in our paper[20], the term $-\partial E / \partial \mathbf{h}$ in Eq.(16) means the net force on some particles in the right half of the crystal by all particles in the left half of the crystal. For any single force of such on a particle, which is vibrating around the equilibrium position as a harmonic oscillator, although the vibration causes the force changing a little bit constantly, the force should be averagely the one in the equilibrium state without vibration, as the force change is proportional to the relative displacement of the particle to its equilibrium position. This means that the averaged change caused by vibrational motion on the forces acting on one half of the crystal by the other half, $-\partial(E_{p,MD,vb}) / \partial \mathbf{h}$, is zero, then the phonon's potential energy $E_{p,MD,vb}$ can be ignored in Eq.(16). Actually, neither kinetic energy nor potential energy of phonons affects Eq.(3). However both of them should be reflected in heat capacity calculation.

Bringing Eq.(35) into Eq.(10) then into Eq.(16) (and Eq.(6)), regardless of other kinetic energy, it shows that the period vectors should change if the temperature is changed while keeping the external stress fixed. This thermal expansion by pure harmonic vibrating phonons is contrary to some researcher's ideas.

The calculation should be feasible by employing Debye-Slater model[10] for an example, where the total energy of phonons is

$$E_{t,MD,vb} = \frac{9}{8} nk \Theta_D + 3nkTD \left(\frac{\Theta_D}{T} \right), \quad (36)$$

where Θ_D is Debye temperature and function $D(\dots)$ is Debye integral

$$D(x) = \frac{3}{x^3} \int_0^x \frac{y^3}{e^y - 1} dy. \quad (37)$$

Then the total kinetic energy of phonons per cell $E_{k,MD,vb} = \frac{1}{2} E_{t,MD,vb}$ can be brought into Eq.(16).

VI. SYSTEM COLLAPSE

Careful inspection on Eq.(16) (also based on Eq.(6)) shows that actually the temperature effect, the first term on the left side of Eq.(16), is to try to “break” the crystals, i.e. playing a repulsive role inside the system, then particles inside the system should attract each other enough to overcome it in order to keep crystal stable. However, there is a limit to the overall attraction inside the crystal (the middle term of the left side of Eq.(16)). For fixed external stress, if the temperature is increased so much that its repulsive effect is bigger than the internal attraction limit and the external stress compensation, the crystal will collapse, where Eq.(16) can no longer be satisfied. On the other hand, for whatever temperature, if the external stress is stretching and bigger than the internal attraction limit, the system will also collapse. The higher temperature, the less stretching is needed to break the crystal system.

VII. SUMMARY

By employing Newton’s second law on particles in a cell and applying the dynamical equation of period vectors, crystal structures can be predicted. Not only the action of the external stress/pressure is presented in these equations, but also that of the (external) temperature via the kinetic energy term of the internal stress. They are actually equations of state of crystals in a microscopic form, then thermodynamical properties and processes can be calculated as well. Contrary to usual ideas, the equations show that pure harmonic vibrating phonons can explain thermal expansion in crystals when temperature is changed. Furthermore crystals are also shown to collapse when the equations can not be satisfied.

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