Article

Equation of State under External Stress from Crystals to Non-Crystals

Gang Liu *

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Equation of State Under External Stress from Crystals to Non-Crystals

Gang Liu

Independent Researcher, Kingston, Ontario, Canada; gl.cell@outlook.com

Abstract

The equation of state of crystals under external stress, derived years ago based on the principles of statistical physics, was re-derived in the same way, but for non-crystals under general external stress and temperature. Its relationship with the macroscopic mechanical equilibrium condition was also discussed.

Keywords: equation of state; external stress; non-crystals

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1. Introduction

The Equation of State (EOS) of a system has a very long history, with the first publication in 1662 [1]. The main purpose of it is to yield the specific fixed volume of a given amount of material under any given external mechanical and thermal conditions. Then, the system must be in a macroscopic equilibrium state.

In fact, the rigorous EOS for any material system can be derived based on the following widely used *de facto* "theorem" in Statistical Physics, which reflects the first law of thermodynamics. As shown with the Equations (2.95), (3.3), and (3.129) of the statistical thermodynamics book [2] by Bellac, Mortessagne, and Batrouni, the "theorem" may be stated as:

Suppose that the infinitesimal work done by the external forces on a system in a macroscopic equilibrium state can be written in the form of

$$dW = A_1 dB_1 + A_2 dB_2 + \cdots + A_m dB_m, \tag{1}$$

where B_1, B_2, $\cdots$, and B_m are variables independent of each other. Then, for any pair of the conjugate variables A_i and B_i, one has

$$A_i = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial B_i} \quad (i = 1, 2, \cdots, m), \tag{2}$$

where Z is the partition function of the system, and $\beta = 1/(kT)$ with the Boltzmann constant k and the temperature T (another independent variable).

Now let us consider such a system but under isotropic external pressure P. Then the infinitesimal work done by the external force is

$$dW = -PdV, \tag{3}$$

where V is the system volume. Then, based on the above "theorem", we have the EOS of the system immediately:

$$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}. \tag{4}$$

This EOS, which applies to any system under external isotropic pressure and temperature, is taught in almost all related books [2,3].

2. Crystals Under External Anisotropic Mechanical Conditions

2.1. Crystal Period Vectors and External Stress

A crystal is made of a three-dimensional periodic arrangement of the same cells concisely and tidily. Each cell, containing the same particles, is a parallelepiped. Since a crystal is essentially such an unlimited periodic structure, let us call the edge vectors of the cells as the (crystal) period vectors, shown as **a**, **b**, and **c** red arrows in Figure 1.

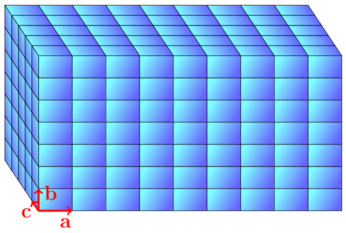

Figure 1. A crystal is made of the same cells tidily, concisely, and infinitely. The red cell edge vectors **a**, **b**, and **c** are also the period vectors of its periodic structure.

The positions of all particles inside the cell, and the crystal period vectors are usually measured through X-ray diffraction experiments. From the pure theory point of view, the particles' positions can also be calculated by applying the Newtonian Dynamics or Quantum Mechanics. Then what is the theory to calculate the period vectors? Furthermore, crystals may be acted by rather complicated external forces. For example, in order to get electric or magnetic field, an additional external pressure is applied onto piezoelectric or piezomagnetic crystals, but in only one direction. As a result, the total external pressures are not the same in all directions. Since the EOS of Equation (4), for an isotropic pressure, accepting only one pressure value, cannot apply in this situation.

Crystals may experience external forces containing components parallel to the crystal surfaces, as shown in Figure 2. In general, external forces can be described by the so-called stress. Like pressure (the normal force per unit area), roughly speaking, stress is the total force acting on a surface per unit area "vector". It is expressed as a second-rank tensor (3×3 matrix). The force by the stress **S** acting on the area vector **œ** of a surface is **S** · **œ**. For crystals in equilibrium states, the external stress must be symmetric.

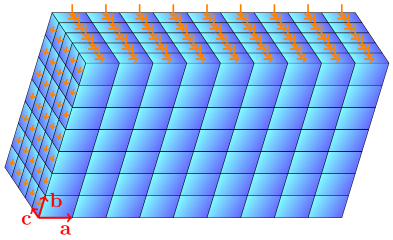

Figure 2. The crystal and its cells in the previous figure deform when external forces with components parallel to its surfaces are applied on it (the red arrows, other than the period vectors). The period vectors **a**, **b**, and **c**, describing the shapes and volumes of the cells, are also changed.

Still as shown in Figure 2, the crystal period vectors may change independently with each other according to the external stress **S** applied. As the period vectors determine the shape and volume of the cells, then proportional to the macroscopic shape and volume of crystals, the equation determining the period vectors is also the EOS of the crystals. It was derived based on the above *de facto* "theorem" for general external stress in our recent effort [4]. We will briefly reiterate it as follows.

2.2. The Derivation of the EOS

Now let us write the infinitesimal work done by the external stress **S** equivalently acting on the surfaces of a crystal cell, which is proportional to that on the surfaces of the whole crystal:

$$dW = (\mathbf{S}\cdot \text{œ}_{\mathbf{a}})\cdot \mathrm{d}\mathbf{a} + (\mathbf{S}\cdot \text{œ}_{\mathbf{b}})\cdot \mathrm{d}\mathbf{b} + (\mathbf{S}\cdot \text{œ}_{\mathbf{c}})\cdot \mathrm{d}\mathbf{c}, \tag{5}$$

where $\text{œ}_{\mathbf{a}} = \mathbf{b}\times\mathbf{c}$, $\text{œ}_{\mathbf{b}} = \mathbf{c}\times\mathbf{a}$, and $\text{œ}_{\mathbf{c}} = \mathbf{a}\times\mathbf{b}$ are surface area vectors of the cell.

Then, according to the above *de facto* “theorem", we have the following equation to determine the period vectors, which is also the EOS for crystals under general external stress and temperature:

$$\mathbf{S}\cdot \text{œ}_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{6}$$

2.3. Tuckerman’s Internal Stress

In 2010, Tuckerman introduced the (macroscopic) internal stress $\mathbf{P}^{(\mathrm{int})}$ of crystals as Equation (5.6.9) in his book [5] (Equation (5.7.9) in the 2023 version):

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

Combining it with Equation (6) yields

$$\mathbf{S}\cdot \text{œ}_{\mathbf{h}} = -\mathbf{P}^{(\mathrm{int})}\cdot \text{œ}_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{8}$$

which means

$$\mathbf{S} + \mathbf{P}^{(\mathrm{int})} = 0. \tag{9}$$

So Equation (6) is the macroscopic mechanical equilibrium condition (MMEC): the macroscopic internal stress balances the external stress.

2.4. Isotropic External Pressure

The isotropic external pressure P is a special case of the general external stress when the external stress **S** becomes $-P\mathbf{I}$, with **I** being the identity tensor. Then, Equation (6) becomes

$$-P\text{œ}_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{10}$$

which can be further written as

$$PV = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{h}}\right)\cdot \mathbf{h} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{11}$$

Since the external pressure is the same in all directions, we may assume that the crystal cell expands uniformly when the external pressure changes. This means that all the directions of the period vectors are fixed and their magnitudes are proportional to $V^{1/3}$. In other words, the period vectors depend on the volume only by containing the factor $V^{1/3}$. Once the factor $V^{1/3}$ is removed, the period vectors are independent of the volume V:

$$\frac{\partial}{\partial V}\left(\frac{\mathbf{h}}{V^{\frac{1}{3}}}\right) = 0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{12}$$

As a result,

$$\frac{\partial \mathbf{h}}{\partial V} = \frac{\partial}{\partial V}\left(\frac{\mathbf{h}}{V^{\frac{1}{3}}}V^{\frac{1}{3}}\right) = \left(\frac{\mathbf{h}}{V^{\frac{1}{3}}}\right)\frac{\partial V^{\frac{1}{3}}}{\partial V} = \frac{1}{3V}\mathbf{h} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{13}$$

Then using Equation (13) and Equation (11),

$$\frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{1}{\beta}\sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}}\left(\frac{\partial \ln Z}{\partial \mathbf{h}}\right)\cdot\frac{\partial \mathbf{h}}{\partial V} = \frac{1}{3V\beta}\sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}}\left(\frac{\partial \ln Z}{\partial \mathbf{h}}\right)\cdot\mathbf{h} = P. \tag{14}$$

It reproduces Equation (4). Therefore, Equation (6) covers the special case of the isotropic external pressure.

It is better to put Equations (14) and (11) together as a summary for the external isotropic pressure condition:

$$\begin{aligned}
P &= \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)\frac{V}{V}, \\
P &= \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{a}}\right)\cdot\frac{\mathbf{a}}{V}, \\
P &= \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{b}}\right)\cdot\frac{\mathbf{b}}{V}, \\
P &= \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{c}}\right)\cdot\frac{\mathbf{c}}{V}.
\end{aligned} \tag{15}$$

In fact, all these four equations must be satisfied at the same time, and they are satisfied as long as any one of them is satisfied and the crystal expands uniformly with the external isotropic pressure P.

3. Non-Crystals Under General External Stress

3.1. The EOS

Assuming that the basic physical properties of a non-crystal system do not depend on its macroscopic shape, the system may be regarded as only one, albeit huge, crystal "cell" without periodicity in structure, and the "period vectors" are now only the edge vectors of the "cell", but we may still call them the period vectors.

Since the forces of the external stress on the system surfaces are distributed uniformly, the system can be assumed to always maintain a parallelepiped shape, if not broken. Then using the same symbols, Equation (5) is the infinitesimal work done by the external stress **S** acting on the surfaces of the system, then we also obtain Equation (6) as the EOS.

Supposing that the Tuckerman's internal stress, as in Equation (7), also applies, the MMEC as of Equation (9) holds as well. Furthermore, since Equations (10)–(15) apply, the special case of isotropic external pressure is covered.

3.2. The Detailed MMEC in Classical Physics

In classical physics, the partition function can be factorized as:

$$Z = Z_k Z_u, \tag{16}$$

where Z_k and Z_u are contributed by the kinetic energy E_k and the potential energy E_p of the system, respectively. As in Equations (3.45)–(3.47) in the statistical reference book [2], they can be further expressed as:

$$Z_k = \frac{V^N}{N!}\int\int\cdots\int\frac{1}{h^{3N}}e^{-\beta E_k(\mathbf{p})}\mathrm{d}\mathbf{p}, \tag{17}$$

$$Z_u = \frac{1}{V^N}\int_V\int_V\cdots\int_V e^{-\beta E_p(\mathbf{R})}\mathrm{d}\mathbf{R}, \tag{18}$$

where h is the Planck constant and N is the total number of particles in the system. The integration is over all particle momenta $\mathbf{p} = \{\mathbf{p}_1, \mathbf{p}_2, \cdots, \mathbf{p}_N\}$ in Equation (17), and over all particle positions $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N\}$ within the system volume for Equation (18).

Then, Equation (6) becomes

$$\mathbf{S}\cdot\textbf{œ}_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z_k}{\partial \mathbf{h}} - \frac{1}{\beta}\frac{\partial \ln Z_u}{\partial \mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \tag{19}$$

3.2.1. The Thermal Pressure

Since the integration in Equation (17) has nothing to do with the period vectors, the first term on the right side of Equation (19), the derivative of the partition function contributed by the kinetic energy, can be written as:

$$-\frac{1}{\beta}\frac{\partial \ln Z_k}{\partial \mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln\left(V^N\right)}{\partial \mathbf{h}} = -\frac{1}{\beta}\frac{N}{V}\frac{\partial V}{\partial \mathbf{h}} = -\frac{N}{V}kT\textbf{œ}_{\mathbf{h}} = -P_{thermal}\textbf{œ}_{\mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \tag{20}$$

This is the thermal pressure $P_{thermal} = \frac{N}{V}kT$ on the cell surfaces, reflecting the forces in the particle collisions and/or the “force associated with the transport of momentum" mentioned in our earlier work [6].

3.2.2. The Derivative of Partition Function of Potential Contribution with Respect to the Period Vectors

Now, let us take the derivative of the partition function contributed by the potential energy, the second term on the right side of Equation (19), by using of Equation (18):

$$-\frac{1}{\beta}\frac{\partial \ln Z_u}{\partial \mathbf{h}} = -\frac{1}{\beta Z_u}\frac{\partial}{\partial \mathbf{h}}Z_u \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \tag{21}$$

Here, the derivative is with respect to the period vectors, which determine the volume V of the “cell", also the region of the integrals in Equation (18). A careful inspection shows that Equation (18) is the average of the function $e^{-\beta E_p(\mathbf{R})}$, which depends on the particle positions $\mathbf{R}$, evenly and fully sampled over the “cell" space Vs. Then, as long as the points $\mathbf{R}$ are sampled in exactly the same way, the calculated average is the same, even if the integrals are changed in some form, from a physics point of view. In any case, we will derive it rigorously, in view of mathematics, as follows.

First, let us consider a general position vector $\mathbf{r}$ in the “cell", expanded as $\mathbf{r} = r_{\mathbf{a}}\mathbf{a} + r_{\mathbf{b}}\mathbf{b} + r_{\mathbf{c}}\mathbf{c}$ with $r_{\mathbf{h}} = \frac{1}{V}\mathbf{r}\cdot\textbf{œ}_{\mathbf{h}}$ for $\mathbf{h} = \mathbf{a}, \mathbf{b}$, or $\mathbf{c}$. Imagine evenly cutting the “cell" into n blocks along the period vector $\mathbf{a}$ with geometric planes parallel to the surface $\textbf{œ}_{\mathbf{a}}$, m blocks along $\mathbf{b}$ with geometric planes parallel to $\textbf{œ}_{\mathbf{b}}$, and l blocks along $\mathbf{c}$ with geometric planes parallel to $\textbf{œ}_{\mathbf{c}}$. By the integral definition, for any function $f(\mathbf{r})$, we have

$$\begin{aligned}\frac{1}{V}\int_V f(\mathbf{r})\mathrm{d}\mathbf{r} &= \frac{1}{V}\lim_{\substack{n\to\infty\\ m\to\infty\\ l\to\infty}}\sum_{i=1}^{n}\sum_{j=1}^{m}\sum_{k=1}^{l} f\left(\mathbf{r}_{i,j,k}\right)\Delta v_{i,j,k}\\ &= \lim_{\substack{n\to\infty\\ m\to\infty\\ l\to\infty}}\sum_{i=1}^{n}\sum_{j=1}^{m}\sum_{k=1}^{l} f\left(\mathbf{r}_{i,j,k}\right)\frac{\Delta v_{i,j,k}}{V},\end{aligned} \tag{22}$$

where $\Delta v_{i,j,k}$ is the volume of the tiny intersection of the i-th block along $\mathbf{a}$, j-th block along $\mathbf{b}$, and k-th block along $\mathbf{c}$, and $\mathbf{r}_{i,j,k}$ is the center position of the intersection. In fact, under the limit of n, m, and l all approaching infinity, $\Delta v_{i,j,k}$ means the term $\mathrm{d}\mathbf{r}$ of the integral of the left side expression of the above equation in mathematics. Meanwhile, the expression $\frac{\Delta v_{i,j,k}}{V}$ in the above equation corresponds to the term $\mathrm{d}r_{\mathbf{a}}\mathrm{d}r_{\mathbf{b}}\mathrm{d}r_{\mathbf{c}}$ in the three nested integrals all from 0 to 1 in the next equation, so we have it based on the above equation and the integral definition as:

$$\begin{aligned}\frac{1}{V}\int_V f(\mathbf{r})\mathrm{d}\mathbf{r} &= \int_0^1\int_0^1\int_0^1 f(\mathbf{r})\mathrm{d}r_{\mathbf{a}}\mathrm{d}r_{\mathbf{b}}\mathrm{d}r_{\mathbf{c}} \\ &= \int_0^1\int_0^1\int_0^1 f(\mathbf{r}(r_{\mathbf{a}},r_{\mathbf{b}},r_{\mathbf{c}}))\mathrm{d}r_{\mathbf{a}}\mathrm{d}r_{\mathbf{b}}\mathrm{d}r_{\mathbf{c}}. \end{aligned} \tag{23}$$

Please note that the $f(\mathbf{r})$ remains the same function of the position vector $\mathbf{r}$ here. However, the position $\mathbf{r}$ is not an independent variable now, but a further function of $(r_{\mathbf{a}},r_{\mathbf{b}},r_{\mathbf{c}})$, as $\mathbf{r}=r_{\mathbf{a}}\mathbf{a}+r_{\mathbf{b}}\mathbf{b}+r_{\mathbf{c}}\mathbf{c}$.

Now let us also expand the position vector of each particle in the "cell", with respect to the period vectors as:

$$\mathbf{r}_i = r_{i,\mathbf{a}}\mathbf{a}+r_{i,\mathbf{b}}\mathbf{b}+r_{i,\mathbf{c}}\mathbf{c} \qquad (i=1,\cdots,N), \tag{24}$$

where the corresponding scaled coordinates $r_{i,\mathbf{h}}$, in the range of $[0,1)$, are also of the same form

$$r_{i,\mathbf{h}} = \frac{1}{V}\mathbf{r}_i\cdot\text{œ}_{\mathbf{h}} \quad (i=1,\cdots,N;\ \mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \tag{25}$$

Since Equation (23) applies to every particles, employing Equation (24) to map all scaled coordinates to the corresponding actual particle position vectors $\mathbf{R}$ in the system potential energy $E_p(\mathbf{R})$, the samplings and the average of $e^{-\beta E_p(\mathbf{R})}$ keep unchanged, even when Equation (18) is rewritten as:

$$Z_u = \int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\cdots\int_0^1\int_0^1\int_0^1 e^{-\beta E_p(\mathbf{R})} \\ \mathrm{d}r_{1,\mathbf{a}}\mathrm{d}r_{1,\mathbf{b}}\mathrm{d}r_{1,\mathbf{c}}\mathrm{d}r_{2,\mathbf{a}}\mathrm{d}r_{2,\mathbf{b}}\mathrm{d}r_{2,\mathbf{c}}\cdots\mathrm{d}r_{N,\mathbf{a}}\mathrm{d}r_{N,\mathbf{b}}\mathrm{d}r_{N,\mathbf{c}}. \tag{26}$$

Since the integrals are of fixed regions now, the derivative can go inside

$$\begin{aligned}\frac{\partial Z_u}{\partial\mathbf{h}} &= \int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\cdots\int_0^1\int_0^1\int_0^1 \frac{\partial}{\partial\mathbf{h}}e^{-\beta E_p(\mathbf{R})} \\ &\qquad \mathrm{d}r_{1,\mathbf{a}}\mathrm{d}r_{1,\mathbf{b}}\mathrm{d}r_{1,\mathbf{c}}\mathrm{d}r_{2,\mathbf{a}}\mathrm{d}r_{2,\mathbf{b}}\mathrm{d}r_{2,\mathbf{c}}\cdots\mathrm{d}r_{N,\mathbf{a}}\mathrm{d}r_{N,\mathbf{b}}\mathrm{d}r_{N,\mathbf{c}} \\ &= \int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\cdots\int_0^1\int_0^1\int_0^1 -\beta e^{-\beta E_p(\mathbf{R})}\frac{\partial}{\partial\mathbf{h}}E_p(\mathbf{R}) \\ &\qquad \mathrm{d}r_{1,\mathbf{a}}\mathrm{d}r_{1,\mathbf{b}}\mathrm{d}r_{1,\mathbf{c}}\mathrm{d}r_{2,\mathbf{a}}\mathrm{d}r_{2,\mathbf{b}}\mathrm{d}r_{2,\mathbf{c}}\cdots\mathrm{d}r_{N,\mathbf{a}}\mathrm{d}r_{N,\mathbf{b}}\mathrm{d}r_{N,\mathbf{c}} \qquad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \end{aligned} \tag{27}$$

Here the particle positions $\mathbf{R}$ are not independent variables, but expressed as in Equation (24). In a Cartesian coordinate system, the components of the period vector $\mathbf{h}$ may be denoted as (h_x,h_y,h_z). Employing Equation (24), one has

$$\frac{\partial\mathbf{r}_i}{\partial h_x} = (r_{i,\mathbf{h}},0,0),\ \frac{\partial\mathbf{r}_i}{\partial h_y} = (0,r_{i,\mathbf{h}},0),\ \frac{\partial\mathbf{r}_i}{\partial h_z} = (0,0,r_{i,\mathbf{h}})\ \ (i=1,\cdots,N;\ \mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}), \tag{28}$$

and, for any d-direction,

$$\frac{\partial E_p(\mathbf{R})}{\partial h_d} = \sum_{i=1}^{N}\frac{\partial E_p(\mathbf{R})}{\partial\mathbf{r}_i}\cdot\frac{\partial\mathbf{r}_i}{\partial h_d} \quad (d=x,y,z;\ \mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \tag{29}$$

Let us denote the net force acting on particle i by all other particles as:

$$\mathbf{F}_i = -\frac{\partial E_p(\mathbf{R})}{\partial\mathbf{r}_i}, \tag{30}$$

with component form of $\left(F_{i,x}, F_{i,y}, F_{i,z}\right)$, and use Equations (25), (28)–(30) to get:

$$\begin{aligned}
\frac{\partial E_p(\mathbf{R})}{\partial \mathbf{h}} &= \left(\frac{\partial}{\partial h_x}, \frac{\partial}{\partial h_y}, \frac{\partial}{\partial h_z}\right) E_p(\mathbf{R}) \\
&= \sum_{i=1}^{N} \left(-F_{i,x} r_{i,\mathbf{h}},\ -F_{i,y} r_{i,\mathbf{h}},\ -F_{i,z} r_{i,\mathbf{h}}\right) \\
&= \sum_{i=1}^{N} (-\mathbf{F}_i) r_{i,\mathbf{h}} = \sum_{i=1}^{N} (-\mathbf{F}_i) \frac{\mathbf{r}_i \cdot \mathbf{\oe}_{\mathbf{h}}}{V} \\
&= -\frac{1}{V} \sum_{i=1}^{N} (\mathbf{F}_i \otimes \mathbf{r}_i) \cdot \mathbf{\oe}_{\mathbf{h}} \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}).
\end{aligned} \tag{31}$$

Since the derivatives are clear now, let us go back to the "cell" spaces for the integration and use Equations (27) and (31), to rewrite Equation (21) as:

$$-\frac{\partial \ln Z_u}{\beta \partial \mathbf{h}} = \frac{1}{Z_u V^N} \int_V \int_V \cdots \int_V e^{-\beta E_p(\mathbf{R})} \left(-\frac{1}{V} \sum_{i=1}^{N} \mathbf{F}_i \otimes \mathbf{r}_i \cdot \mathbf{\oe}_{\mathbf{h}}\right) \mathrm{d}\mathbf{R} \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{32}$$

This is the average of Equation (31) for all possible positions of particles, with the weight of $e^{-\beta E_p(\mathbf{R})}$, but normalized.

3.2.3. The Pair-Interaction Contributions

If only consider internal pair-interactions, Equation (31) can be explicitly rewritten as:

$$\frac{\partial E_p(\mathbf{R})}{\partial \mathbf{h}} = -\frac{1}{V} \sum_{i=1}^{N} (\mathbf{F}_i \otimes \mathbf{r}_i) \cdot \mathbf{\oe}_{\mathbf{h}} = -\frac{1}{V} \sum_{i=1}^{N} \sum_{j \neq i}^{N} (\mathbf{f}_{j\to i} \otimes \mathbf{r}_i) \cdot \mathbf{\oe}_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{33}$$

where $\mathbf{f}_{j\to i}$ is the force acting on particle i by particle j. Since $\mathbf{f}_{j\to i} + \mathbf{f}_{i\to j} = 0$, we have

$$\begin{aligned}
\frac{\partial E_p(\mathbf{R})}{\partial \mathbf{h}} &= -\frac{1}{2V} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left(\mathbf{f}_{j\to i} \otimes \mathbf{r}_i + \mathbf{f}_{i\to j} \otimes \mathbf{r}_j\right) \cdot \mathbf{\oe}_{\mathbf{h}} \\
&= -\frac{1}{2V} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left(\mathbf{f}_{j\to i} \otimes \left(\mathbf{r}_i - \mathbf{r}_j\right)\right) \cdot \mathbf{\oe}_{\mathbf{h}} \\
&= -\frac{1}{V} \sum_{i=1}^{N-1} \sum_{j > i}^{N} \left(\mathbf{f}_{i\to j} \otimes \left(\mathbf{r}_j - \mathbf{r}_i\right)\right) \cdot \mathbf{\oe}_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}).
\end{aligned} \tag{34}$$

Let us consider all geometric planes cutting through the "cell" but parallel to $\mathbf{\oe}_{\mathbf{h}}$. The total amount of the planes may be defined as $\mathbf{h} \cdot \mathbf{\oe}_{\mathbf{h}} = V$, as it is proportional to the length of the period vector $\mathbf{h}$. Then, between particles j and i, there are $\left|\left(\mathbf{r}_i - \mathbf{r}_j\right) \cdot \mathbf{\oe}_{\mathbf{h}}\right| \leq V$ amount of such planes, which the force $\mathbf{f}_{i\to j}$ penetrates and only penetrates. Thus, the term in the above equation

$$-\frac{1}{V}\left(\mathbf{f}_{i\to j} \otimes \left(\mathbf{r}_j - \mathbf{r}_i\right)\right) \cdot \mathbf{\oe}_{\mathbf{h}} = \frac{\left(\mathbf{r}_i - \mathbf{r}_j\right) \cdot \mathbf{\oe}_{\mathbf{h}}}{V} \mathbf{f}_{i\to j} \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{35}$$

means the two particles' contribution to the interaction between the left and the right sides of each of the planes, but averaged over all the planes. This is similar to the Irving-Kirkwood expression [7].

3.2.4. The Many-Body Interaction Contributions

In actual calculations, three-, four-, and/or even more-body interactions [8–10] may also be employed, as in molecular dynamics simulations. By definition, these interactions mean that any of the forces depend on the positions of all the participating particles, then can not be normally replaced with some pair-interactions in general. Newton's Third Law may be interpreted as: within a given system, any part may exert force(s) on any other part(s), but cannot accelerate the system itself as a whole, then the net of all forces and the net of all torques of all participating particles must be zero. For example, for an M-body interaction ($M \geq 2$), we have

$$\sum_{k=1}^{M} \mathbf{F}_k^{(M)} = 0, \tag{36}$$

where $\mathbf{F}_k^{(M)}$ is the M-body force on particle k by the rest $M-1$ particles.

If an internal M-body interaction is employed, all the corresponding M-body potentials of various groups of M particles may be included in the system potential $E_p(\mathbf{R})$ of Equation (18). Then all the forces of each group additionally contribute to Equation (32), in the form of

$$\begin{aligned}
&\left(-\frac{1}{V} \sum_{k=1}^{M} \mathbf{F}_k^{(M)} \otimes \mathbf{r}_k \cdot \boldsymbol{\oe}_{\mathbf{h}} \right) \\
&= -\frac{1}{V} \left(\mathbf{F}_1^{(M)} \otimes \mathbf{r}_1 + \sum_{k=2}^{M} \mathbf{F}_k^{(M)} \otimes \mathbf{r}_k \right) \cdot \boldsymbol{\oe}_{\mathbf{h}} \\
&= -\frac{1}{V} \left(-\sum_{k=2}^{M} \mathbf{F}_k^{(M)} \otimes \mathbf{r}_1 + \sum_{k=2}^{M} \mathbf{F}_k^{(M)} \otimes \mathbf{r}_k \right) \cdot \boldsymbol{\oe}_{\mathbf{h}} \\
&= \left(-\frac{1}{V} \sum_{k=2}^{M} \mathbf{F}_k^{(M)} \otimes (\mathbf{r}_k - \mathbf{r}_1) \cdot \boldsymbol{\oe}_{\mathbf{h}} \right) \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}),
\end{aligned} \tag{37}$$

where Equation (36) was employed.

Compared with Equation (34), Equation (37) may mean an M-body interaction can be instantaneously regarded as $M-1$ pair-interactions here. In each of the $M-1$ pairs, the net of the two forces is zero. However, they may not point to each other. Although they may have non-zero net torque, the total torque of the M-body interaction is zero, as required by the Newton's Third Law. Then, the M-body interactions contribute the forces over the previously mentioned geometric planes the same way as pair-interactions do.

3.2.5. Conclusions

According to Equations (20), (32), (34), (35), and (37), the right side of Equation (19) is the internal forces between the two sides of geometric planes cutting through the system but parallel to the system surface $\boldsymbol{\oe}_{\mathbf{h}}$, then averaged over all the planes and over all possible particle position distributions, while the left side is the external force on the surface $\boldsymbol{\oe}_{\mathbf{h}}$, then Equation (19) means the MMEC.

4. Summary

Equation (6) is the EOS of both crystals and non-crystals in macroscopic equilibrium states under general external symmetric stress, covering the special case of isotropic pressure, and a positive temperature. It can be explicitly shown in classical statistical physics that Equation (6) is also the macroscopic mechanical equilibrium condition of the system.

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References

1. J. B. West, *J. Appl. Physiol.*, **98**, 31-39 (2005), https://doi.org/10.1152/japplphysiol.00759.2004
2. M.L. Bellac, F. Mortessagne, G.G. Batrouni, *Equilibrium and Non-equilibrium Statistical Thermodynamics* (Cambridge University Press, Cambridge, 2004)
3. O.L. Anderson, *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford University Press, Oxford, 1995)
4. G. Liu, *Eur. Phys. J. Plus* **136**, 48 (2021), https://doi.org/10.1140/epjp/s13360-020-01010-6 https://doi.org/10.20944/preprints201904.0076.v10
5. M.E. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, Oxford, 2010)
6. G. Liu, *Can. J. Phys.*, **93**, 974-978 (2015), arXiv:cond-mat/0209372v16, https://dx.doi.org/10.1139/cjp-2014-0518
7. J. H. Irving and J. G. Kirkwood, *The Journal of Chemical Physics* **18**, 817 (1950), http://dx.doi.org/10.1063/1.1747782
8. G. Liu, Preprints.org 2017, 2017090030, https://doi.org/10.20944/preprints201709.0030.v2
9. G. Liu, E. G. Wang, D. S. Wang, *Chinese Phys. Lett.* **14**, 764 (1997), https://doi.org/10.1088/0256-307X/14/10/012
10. G. Liu, E. G. Wang, *Solid State Commun.* **105**, 671 (1998), https://doi.org/10.1016/S0038-1098(98)00001-5