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Equation of State Under External Stress from Crystals to Non-Crystals (the Third Version)

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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 long history, with its first publication in 1662[1]. The main purpose is to yield the specific fixed volume of a given amount of material under any given external mechanical and thermal conditions. Thus, the system must be in a macroscopic equilibrium state. While the rigorous EOS of any material under the special case of external isotropic pressure is well known, and the one for general external stress has been derived for crystals in recent years, this article derives such an EOS for non-crystals under external stress.

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 in 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 follows:

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

$$\mathrm{d}W = A_1 \mathrm{d}B_1 + A_2 \mathrm{d}B_2 + \cdots + A_m \mathrm{d}B_m, \tag{1}$$

where B_1, B_2, $\cdots$, and B_m are independent variables. Then, for any pair of the conjugate variables A_i and B_i, we have:

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

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

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

$$\mathrm{d}W = -P\mathrm{d}V, \tag{3}$$

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

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

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 composed of a concise and tidy three-dimensional periodic arrangement of identical cells. Each cell, containing the same set of particles, has the shape of a parallelepiped. For its periodic structure, let us call the three independent edge vectors **a**, **b**, and **c** of a cell the (crystal) period vectors. They form a right-handed triad, shown as the red arrows in Figure 1.

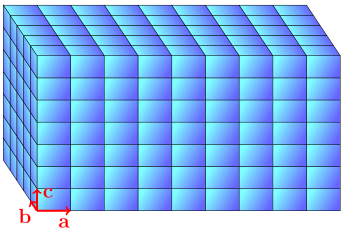

Figure 1. A crystal consists of an infinite and periodic arrangement of identical unit cells. The edge vectors of a cell, denoted by **a**, **b**, and **c**, shown as red arrows, are the period vectors of the crystal structure.

The positions of all particles within a unit cell, as well as the crystal period vectors, are typically determined experimentally using X-ray diffraction. From a theoretical standpoint, the particle positions can be obtained by applying either classical Newtonian dynamics or quantum mechanical methods. A natural question then arises: what theoretical framework determines the period vectors?

In fact, crystals may be subjected to complex external forces. For example, in order to induce electric or magnetic fields in piezoelectric or piezomagnetic materials, additional external pressure may be applied along a specific direction, but only in that direction. As a result, the external pressures acting on the crystal differ along different directions. Under such conditions, the EOS given in Equation (4), which assumes isotropic pressure characterized by a single scalar value, is not applicable.

Figure 2 illustrates a situation in which the crystals are subjected to external forces with components parallel to their surfaces. In general, external forces can be described by the concept of *stress*. Analogous to pressure (the normal force per unit area), stress represents the force acting on a surface per unit area vector. It is formally expressed as a second-rank tensor (a 3×3 matrix). The force exerted by the external stress tensor **S** on a surface with area vector **œ** is given by **S** · **œ**. For a crystal in mechanical equilibrium, the external stress tensor must be symmetric.

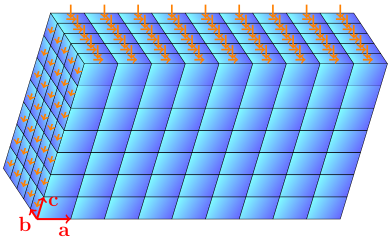

Figure 2. The crystal and its cells in the previous figure undergo deformation, especially when external forces with components parallel to its surfaces are applied on it (the red arrows, other than the period vectors). Consequently, the period vectors **a**, **b**, and **c**, describing the shapes and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

Still as shown in Figure 2, the crystal period vectors may vary independently in response to the applied external stress **S**. Since these vectors determine the shape and volume of the unit cell—and, correspondingly, the macroscopic shape and volume of the crystal—the equations governing the period vectors effectively constitute the EOS of the crystal. Such an EOS, applicable to general external stress, was derived in our recent work [4] based on the above *de facto* "theorem". For completeness, we briefly outline the main results below first.

2.2. The Derivation of the EOS

Now let us write the infinitesimal work done by the external stress $\mathbf{S}$ equivalently acting on the surfaces of a crystal cell, which is proportional to that on the surfaces of the entire crystal:

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

where $\boldsymbol{œ}_{\mathbf{a}} = \mathbf{b}\times\mathbf{c}$, $\boldsymbol{œ}_{\mathbf{b}} = \mathbf{c}\times\mathbf{a}$, and $\boldsymbol{œ}_{\mathbf{c}} = \mathbf{a}\times\mathbf{b}$ are the 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:

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

2.3. Tuckerman's Internal Stress

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

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

where for crystals, the cell volume is $V = \boldsymbol{œ}_{\mathbf{a}}\cdot\mathbf{a} = \boldsymbol{œ}_{\mathbf{b}}\cdot\mathbf{b} = \boldsymbol{œ}_{\mathbf{c}}\cdot\mathbf{c}$.

Combining it with Equation (6) yields

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

which means

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

So Equation (6) is also 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 $\mathbf{S}$ becomes $-P\mathbf{I}$, with $\mathbf{I}$ being the identity tensor. Then, Equation (6) becomes

$$PV = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{h}}\right)\cdot\mathbf{h} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{10}$$

As the external pressure is the same in all directions, we can 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 only on the volume by containing a factor $V^{1/3}$. Once the factor $V^{1/3}$ is removed, the period vectors are independent of the cell volume V:

$$\frac{\partial}{\partial V}\left(\frac{\mathbf{h}}{V^{\frac{1}{3}}}\right) = 0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{11}$$

As a result,

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

Then using Equation (12) and Equation (10),

$$\frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{1}{\beta}\sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}}\left(\frac{\partial \ln Z}{\partial \mathbf{h}}\right)\cdot\frac{\partial \mathbf{h}}{\partial V} = \frac{1}{3V\beta}\sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}}\left(\frac{\partial \ln Z}{\partial \mathbf{h}}\right)\cdot\mathbf{h} = P. \tag{13}$$

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

It is better to use Equations (10) and (13) as a summary for the external isotropic pressure conditions:

$$\begin{aligned} P &= \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{a}}\right)\cdot\frac{\mathbf{a}}{V}, \\ P &= \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{b}}\right)\cdot\frac{\mathbf{b}}{V}, \\ P &= \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{c}}\right)\cdot\frac{\mathbf{c}}{V}, \\ P &= \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)\frac{V}{V}. \end{aligned} \tag{14}$$

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

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; then, 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 always be assumed to 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; therefore, we also obtain Equation (6) as the EOS of non-crystals.

Supposing that Tuckerman’s internal stress, as in Equation (7), also applies, the MMEC as in Equation (9) also holds. Furthermore, since Equations (10)-(14) 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:

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

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:

$$\begin{aligned} Z_k &= \frac{V^N}{N!}\int\int\cdots\int\frac{1}{h^{3N}}e^{-\beta E_k(\mathbf{p})}\mathrm{d}\mathbf{p}, \qquad (16)\\ Z_u &= \frac{1}{V^N}\int_V\int_V\cdots\int_V e^{-\beta E_p(\mathbf{R})}\mathrm{d}\mathbf{R}, \qquad (17)\end{aligned}$$

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 (16), and over all particle positions $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N\}$ within the system volume for Equation (17). Just a note, although the integral

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variables d$\mathbf{p}$ and d$\mathbf{R}$ in the above two equations are in the form of vectors, they are actually scalars, representing infinitesimal “volumes" around the momenta and positions, respectively.

Then, Equation (6) becomes

$$\mathbf{S}\cdot\boldsymbol{\oe}_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z_k}{\partial \mathbf{h}} - \frac{1}{\beta}\frac{\partial \ln Z_u}{\partial \mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \tag{18}$$

3.2.1. The Thermal Pressure

Since the integration in Equation (16) has nothing to do with the period vectors, the first term on the right-hand side of Equation (18), the derivative of the partition function contributed by the kinetic energy, can be written as:

$$-\frac{1}{\beta}\frac{\partial \ln Z_k}{\partial \mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln\left(V^N\right)}{\partial \mathbf{h}} = -\frac{1}{\beta}\frac{N}{V}\frac{\partial V}{\partial \mathbf{h}} = -P_{thermal}\boldsymbol{\oe}_{\mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \tag{19}$$

This is the thermal pressure $P_{thermal} = \frac{N}{V}kT$ equivalently acting 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 the Partition Function of the 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-hand side of Equation (18), by using of Equation (17):

$$-\frac{1}{\beta}\frac{\partial \ln Z_u}{\partial \mathbf{h}} = -\frac{1}{\beta Z_u}\frac{\partial}{\partial \mathbf{h}}Z_u \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \tag{20}$$

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 (17). A careful inspection showed that Equation (17) is the arithmetic 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 this rigorously, even from the perspective 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 $r_{\mathbf{h}} = \frac{1}{V}\mathbf{r}\cdot\boldsymbol{\oe}_{\mathbf{h}} \in [0,1)$ 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 $\boldsymbol{\oe}_{\mathbf{a}}$, m blocks along $\mathbf{b}$ with geometric planes parallel to $\boldsymbol{\oe}_{\mathbf{b}}$, and l blocks along $\mathbf{c}$ with geometric planes parallel to $\boldsymbol{\oe}_{\mathbf{c}}$. By the integral definition, for any function $f(\mathbf{r})$, we have

$$\frac{1}{V}\int_V f(\mathbf{r})\mathrm{d}\mathbf{r} = \frac{1}{V}\lim_{\substack{n\to\infty\\ m\to\infty\\ l\to\infty}}\sum_{i=1}^{n}\sum_{j=1}^{m}\sum_{k=1}^{l} f\left(\mathbf{r}_{i,j,k}\right)\Delta v_{i,j,k}, \tag{21}$$

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 the vector $\mathbf{r}_{i,j,k}$ is the center position of the intersection. In fact, under the limit of n, m, and l all approaching infinity, $\Delta v_{i,j,k}$ is represented by the term d$\mathbf{r}$ of the integral of the left side expression of the above equation in mathematics.

In another view, cutting the period vector $\mathbf{a}$ can be regarded as evenly cutting $r_{\mathbf{a}}$ into n parts of each length $\Delta r_{\mathbf{a}} = \frac{1}{n}$; then each segment of $\mathbf{a}$ is $\Delta r_{\mathbf{a}}\mathbf{a} = \mathbf{a}\Delta r_{\mathbf{a}}$. Similarly, cutting $\mathbf{b}$ is equivalent to cutting $r_{\mathbf{b}}$ into m parts of each length $\Delta r_{\mathbf{b}} = \frac{1}{m}$; then each segment of $\mathbf{b}$ is $\Delta r_{\mathbf{b}}\mathbf{b}$. And cutting $\mathbf{c}$ is cutting $r_{\mathbf{c}}$ into l parts of each length $\Delta r_{\mathbf{c}} = \frac{1}{l}$; then each segment of $\mathbf{c}$ is $\Delta r_{\mathbf{c}}\mathbf{c}$. Then, we have the specific volume expression:

$$\Delta v_{i,j,k} = ((\Delta r_{\mathbf{a}}\mathbf{a}) \times (\Delta r_{\mathbf{b}}\mathbf{b})) \cdot (\Delta r_{\mathbf{c}}\mathbf{c}) = ((\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c})\Delta r_{\mathbf{a}}\Delta r_{\mathbf{b}}\Delta r_{\mathbf{c}} = V\Delta r_{\mathbf{a}}\Delta r_{\mathbf{b}}\Delta r_{\mathbf{c}}, \tag{22}$$

As a result, Equation (21) becomes

$$\frac{1}{V}\int_V f(\mathbf{r})\mathrm{d}\mathbf{r} = \lim_{\substack{n\to\infty \\ m\to\infty \\ l\to\infty}} \sum_{i=1}^{n}\sum_{j=1}^{m}\sum_{k=1}^{l} f\left(\mathbf{r}_{i,j,k}\right)\Delta r_{\mathbf{a}}\Delta r_{\mathbf{b}}\Delta r_{\mathbf{c}}. \tag{23}$$

Recalling that all $r_{\mathbf{a}}$, $r_{\mathbf{b}}$, and $r_{\mathbf{c}}$ are in the range of $[0,1)$, and applying the integral definition once more, we have

$$\int_0^1\int_0^1\int_0^1 f(\mathbf{r}(r_{\mathbf{a}}, r_{\mathbf{b}}, r_{\mathbf{c}}))\mathrm{d}r_{\mathbf{a}}\mathrm{d}r_{\mathbf{b}}\mathrm{d}r_{\mathbf{c}} = \lim_{\substack{n\to\infty \\ m\to\infty \\ l\to\infty}} \sum_{i=1}^{n}\sum_{j=1}^{m}\sum_{k=1}^{l} f\left(\mathbf{r}_{i,j,k}\right)\Delta r_{\mathbf{a}}\Delta r_{\mathbf{b}}\Delta r_{\mathbf{c}}. \tag{24}$$

Then, combining the above two equations, we arrive at:

$$\frac{1}{V}\int_V f(\mathbf{r})\mathrm{d}\mathbf{r} = \int_0^1\int_0^1\int_0^1 f(\mathbf{r}(r_{\mathbf{a}}, r_{\mathbf{b}}, r_{\mathbf{c}}))\mathrm{d}r_{\mathbf{a}}\mathrm{d}r_{\mathbf{b}}\mathrm{d}r_{\mathbf{c}}. \tag{25}$$

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 expand the position vector of every particle in the “cell", with respect to the period vectors, in the same way as:

$$\mathbf{r}_i = r_{i,\mathbf{a}}\mathbf{a} + r_{i,\mathbf{b}}\mathbf{b} + r_{i,\mathbf{c}}\mathbf{c} \qquad (i = 1, \cdots, N), \tag{26}$$

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

$$r_{i,\mathbf{h}} = \frac{1}{V}\mathbf{r}_i \cdot \boldsymbol{\text{œ}}_{\mathbf{h}} \quad (i = 1, \cdots, N;\ \mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{27}$$

Since Equation (25) applies to every particle, employing Equation (26) to map all scaled coordinates to the corresponding real particle position vectors $\mathbf{R}$ in the system potential energy $E_p(\mathbf{R})$, the samplings and the average of $e^{-\beta E_p(\mathbf{R})}$ remain unchanged, even when Equation (17) is rewritten as:

$$Z_u = \int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\int_0^1 \cdots \int_0^1\int_0^1\int_0^1 e^{-\beta E_p(\mathbf{R})}$$
$$\mathrm{d}r_{1,\mathbf{a}}\mathrm{d}r_{1,\mathbf{b}}\mathrm{d}r_{1,\mathbf{c}}\mathrm{d}r_{2,\mathbf{a}}\mathrm{d}r_{2,\mathbf{b}}\mathrm{d}r_{2,\mathbf{c}} \cdots \mathrm{d}r_{N,\mathbf{a}}\mathrm{d}r_{N,\mathbf{b}}\mathrm{d}r_{N,\mathbf{c}}. \tag{28}$$

Since the integrals are of fixed regions now, the derivative can be taken inside:

$$\frac{\partial Z_u}{\partial \mathbf{h}} = \int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\int_0^1 \cdots \int_0^1\int_0^1\int_0^1 -\beta e^{-\beta E_p(\mathbf{R})}\frac{\partial}{\partial \mathbf{h}}E_p(\mathbf{R})$$
$$\mathrm{d}r_{1,\mathbf{a}}\mathrm{d}r_{1,\mathbf{b}}\mathrm{d}r_{1,\mathbf{c}}\mathrm{d}r_{2,\mathbf{a}}\mathrm{d}r_{2,\mathbf{b}}\mathrm{d}r_{2,\mathbf{c}} \cdots \mathrm{d}r_{N,\mathbf{a}}\mathrm{d}r_{N,\mathbf{b}}\mathrm{d}r_{N,\mathbf{c}} \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{29}$$

Here the particle positions $\mathbf{R}$ are not independent variables, but are expressed as in Equation (26). In the Cartesian coordinate system, the components of the period vector $\mathbf{h}$ are denoted as (h_x, h_y, h_z). Using Equation (26), one has

$$\frac{\partial \mathbf{r}_i}{\partial h_x} = (r_{i,\mathbf{h}}, 0, 0),\ \frac{\partial \mathbf{r}_i}{\partial h_y} = (0, r_{i,\mathbf{h}}, 0),\ \frac{\partial \mathbf{r}_i}{\partial h_z} = (0, 0, r_{i,\mathbf{h}})\ \ (i = 1, \cdots, N;\ \mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{30}$$

and, for any d-direction,

$$\frac{\partial E_p(\mathbf{R})}{\partial h_d} = \sum_{i=1}^{N} \frac{\partial E_p(\mathbf{R})}{\partial \mathbf{r}_i} \cdot \frac{\partial \mathbf{r}_i}{\partial h_d} \qquad (d = x, y, z;\ \mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{31}$$

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

$$\mathbf{F}_i = -\frac{\partial E_p(\mathbf{R})}{\partial \mathbf{r}_i}, \tag{32}$$

with the component form of $(F_{i,x}, F_{i,y}, F_{i,z})$, and use Equations (30)-(32) to obtain:

$$\begin{aligned}
\frac{\partial E_p(\mathbf{R})}{\partial \mathbf{h}} &= \left(\frac{\partial}{\partial h_x}, \frac{\partial}{\partial h_y}, \frac{\partial}{\partial h_z}\right) E_p(\mathbf{R}) \\
&= \sum_{i=1}^{N} \left(-F_{i,x} r_{i,\mathbf{h}},\ -F_{i,y} r_{i,\mathbf{h}},\ -F_{i,z} r_{i,\mathbf{h}}\right) \\
&= -\sum_{i=1}^{N} \mathbf{F}_i r_{i,\mathbf{h}} \qquad\qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}).
\end{aligned} \tag{33}$$

Further using Equation (27), Equation (33) becomes:

$$\frac{\partial E_p(\mathbf{R})}{\partial \mathbf{h}} = -\sum_{i=1}^{N} (\mathbf{F}_i) \frac{\mathbf{r}_i \cdot \mathbf{\oe}_{\mathbf{h}}}{V} = -\frac{1}{V} \sum_{i=1}^{N} (\mathbf{F}_i \otimes \mathbf{r}_i) \cdot \mathbf{\oe}_{\mathbf{h}} \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{34}$$

Since the derivatives are done now, let us go back to the “cell" spaces for the integration and use Equations (29) and (34), to rewrite Equation (20) as:

$$-\frac{\partial \ln Z_u}{\beta \partial \mathbf{h}} = \frac{1}{Z_u V^N} \int_V \int_V \cdots \int_V e^{-\beta E_p(\mathbf{R})} \left(-\frac{1}{V} \sum_{i=1}^{N} \mathbf{F}_i \otimes \mathbf{r}_i \cdot \mathbf{\oe}_{\mathbf{h}}\right) \mathrm{d}\mathbf{R} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{35}$$

This is the average of Equation (34) for all possible positions of particles, with the normalized weight of $e^{-\beta E_p(\mathbf{R})}$.

3.2.3. The Pair-Interaction Contributions

If only internal pair-interactions are considered, Equation (34) can be explicitly rewritten as:

$$\frac{\partial E_p(\mathbf{R})}{\partial \mathbf{h}} = -\frac{1}{V} \sum_{i=1}^{N} \sum_{j \neq i}^{N} (\mathbf{f}_{j\to i} \otimes \mathbf{r}_i) \cdot \mathbf{\oe}_{\mathbf{h}} \ (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{36}$$

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

$$\begin{aligned}
\frac{\partial E_p(\mathbf{R})}{\partial \mathbf{h}} &= -\frac{1}{2V} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left(\mathbf{f}_{j\to i} \otimes \mathbf{r}_i + \mathbf{f}_{i\to j} \otimes \mathbf{r}_j\right) \cdot \mathbf{\oe}_{\mathbf{h}} \\
&= -\frac{1}{2V} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left(\mathbf{f}_{j\to i} \otimes (\mathbf{r}_i - \mathbf{r}_j)\right) \cdot \mathbf{\oe}_{\mathbf{h}} \\
&= -\frac{1}{V} \sum_{i=1}^{N-1} \sum_{j > i}^{N} \left(\mathbf{f}_{i\to j} \otimes (\mathbf{r}_j - \mathbf{r}_i)\right) \cdot \mathbf{\oe}_{\mathbf{h}} \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}).
\end{aligned} \tag{37}$$

Let us consider all geometric planes cutting through the “cell" parallel to $\mathbf{\oe}_{\mathbf{h}}$. The total number of planes can 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 $\left|(\mathbf{r}_j - \mathbf{r}_i) \cdot \boldsymbol{\oe}_{\mathbf{h}}\right| \le V$ number of such planes, which the force $\mathbf{f}_{i\to j}$ penetrates and only penetrates. Thus, the term in the above equation

$$-\frac{1}{V}\left(\mathbf{f}_{i\to j} \otimes (\mathbf{r}_j - \mathbf{r}_i)\right) \cdot \boldsymbol{\oe}_{\mathbf{h}} = -\frac{(\mathbf{r}_j - \mathbf{r}_i) \cdot \boldsymbol{\oe}_{\mathbf{h}}}{V}\mathbf{f}_{i\to j} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{38}$$

indicates the contribution of the two particles to the interaction between the left and right sides of each of the planes, and 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, many-body interactions[8,9] may also be employed, in which any of the forces depend on the positions of all participating particles. Thus, they cannot 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; therefore, the net of all forces and the net of all torques of participating particles must be zero. For example, for an M-body interaction ($M \ge 2$), we have:

$$\sum_{k=1}^{M} \mathbf{f}_k^{(M)} = 0, \quad \text{and} \quad \sum_{k=1}^{M} \mathbf{r}_k \times \mathbf{f}_k^{(M)} = 0, \tag{39}$$

where $\mathbf{f}_k^{(M)}$ is the M-body force on particle k by all the remaining $M-1$ 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 (17). Then, all the forces of each group additionally contribute to Equation (34), in the form of

$$\begin{aligned}
-\frac{1}{V}\sum_{k=1}^{M} \mathbf{f}_k^{(M)} \otimes \mathbf{r}_k \cdot \boldsymbol{\oe}_{\mathbf{h}} &= -\frac{1}{V}\left(\mathbf{f}_1^{(M)} \otimes \mathbf{r}_1 + \sum_{k=2}^{M} \mathbf{f}_k^{(M)} \otimes \mathbf{r}_k\right) \cdot \boldsymbol{\oe}_{\mathbf{h}} \\
&= -\frac{1}{V}\left(-\sum_{k=2}^{M} \mathbf{f}_k^{(M)} \otimes \mathbf{r}_1 + \sum_{k=2}^{M} \mathbf{f}_k^{(M)} \otimes \mathbf{r}_k\right) \cdot \boldsymbol{\oe}_{\mathbf{h}} \\
&= -\frac{1}{V}\sum_{k=2}^{M} \mathbf{f}_k^{(M)} \otimes (\mathbf{r}_k - \mathbf{r}_1) \cdot \boldsymbol{\oe}_{\mathbf{h}} \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}),
\end{aligned} \tag{40}$$

where Equation (39) was employed.

Compared with Equation (37), Equation (40) means that 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 a non-zero net torque, the total torque of the M-body interaction is zero, as required by Newton's Third Law. Then, the M-body interactions contribute forces over the previously mentioned geometric planes in the same way that pair-interactions do.

3.2.5. Conclusion

According to Equations (19), (35)-(40), the right-hand side of Equation (18) represents the internal forces between the two sides of each geometric plane cutting through the system parallel to the system surface $\boldsymbol{\oe}_{\mathbf{h}}$, averaged over all these planes and all possible particle position distributions in the cell. Meanwhile, the left-hand side represents the external force on the surface $\boldsymbol{\oe}_{\mathbf{h}}$. This means that Equation (18) represents the MMEC.

For any plane $\kappa_{\mathbf{a}}\boldsymbol{\oe}_{\mathbf{a}} + \kappa_{\mathbf{b}}\boldsymbol{\oe}_{\mathbf{b}} + \kappa_{\mathbf{c}}\boldsymbol{\oe}_{\mathbf{c}}$, where $\kappa_{\mathbf{a}}$, $\kappa_{\mathbf{b}}$, and $\kappa_{\mathbf{c}}$ are any given real numbers, we have

$$\frac{1}{V}(\boldsymbol{\oe}_{\mathbf{a}} \otimes \mathbf{a} + \boldsymbol{\oe}_{\mathbf{b}} \otimes \mathbf{b} + \boldsymbol{\oe}_{\mathbf{c}} \otimes \mathbf{c}) \cdot (\kappa_{\mathbf{a}}\boldsymbol{\oe}_{\mathbf{a}} + \kappa_{\mathbf{b}}\boldsymbol{\oe}_{\mathbf{b}} + \kappa_{\mathbf{c}}\boldsymbol{\oe}_{\mathbf{c}}) = \kappa_{\mathbf{a}}\boldsymbol{\oe}_{\mathbf{a}} + \kappa_{\mathbf{b}}\boldsymbol{\oe}_{\mathbf{b}} + \kappa_{\mathbf{c}}\boldsymbol{\oe}_{\mathbf{c}}. \tag{41}$$

So, the tensor $\frac{1}{V}(\boldsymbol{\oe}_{\mathbf{a}} \otimes \mathbf{a} + \boldsymbol{\oe}_{\mathbf{b}} \otimes \mathbf{b} + \boldsymbol{\oe}_{\mathbf{c}} \otimes \mathbf{c})$ is the identity $\mathbf{I}$. Then, employing Equations (19), (20), and (33), the Tuckerman's internal stress in classical statistical physics for non-crystals can be specifically expressed as:

$$\mathbf{P}^{(\text{int})} = P_{thermal}\mathbf{I} + \frac{1}{Z_u V^N} \int_V \int_V \cdots \int_V e^{-\beta E_p(\mathbf{R})} \left(-\frac{1}{V} \sum_{i=1}^{N} \mathbf{F}_i \otimes \mathbf{r}_i \right) \mathrm{d}\mathbf{R}; \tag{42}$$

then, Equation (9) still 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 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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Abbreviations

The following abbreviations are used in this manuscript:

EOS	equation of state
MMEC	macroscopic mechanical equilibrium condition

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
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). 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, E.G. Wang, *Solid State Commun.*, **105**, 671 (1998). https://doi.org/10.1016/S0038-1098(98)00001-5
9. G. Liu, Preprints.org 2017, 2017090030. https://doi.org/10.20944/preprints201709.0030.v2