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

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Established Equations of State (for external ISOTROPIC pressure)

Equation of state of crystals under geneal external stress

Equation of state of **NON-CRYSTALS** under geneal external stress

Summary

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Summary

What is the Equation of State (EOS) ?

- A simple answer: an equation to determine the **VOLUME** of a fixed amount of matter under any given external (mechanical and thermal) conditions.
- Since the volume it yields is a specific **UNIQUE** number, the system can always be considered in a macroscopic equilibrium state.

The Established Equations of State

No.	Establishment	Year	the equation of state
1	Boyle–Mariotte law	1662	$pV =$ Constant
2	Charles's law	1780	$V \propto T$
3	Gay-Lussac's Law	1808	$p \propto T$
4	Ideal gas law	1834	$pV = nRT$
5	Van der Waals equation	1873	$\left(p + \frac{a}{v^2}\right)(v - b) = RT$
6	(the rigorous one)		$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$

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Notes:

1, the first four are for thin gases only;
2, the fifth is essentially an empirical one;
3, the sixth (last one) is the rigorous one for all matters;
4, all of them are for external ISOTROPIC pressure only.

Actually, the rigorous equation

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

was derived based on the following *de facto* “theorem” in statistical physics.

A *de facto* "theorem" in statistical physics

If the infinitesimal work done by the **EXTERNAL** forces on the system in a macroscopic equilibrium state is written in the form of

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

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

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

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

This “theorem” is presented in all books of statistical physics.

For example, Equations (2.95), (3.3), and (3.129) of the book *Equilibrium and Non-equilibrium Statistical Thermodynamics* (Cambridge, 2004), by M.L. Bellac, F. Mortessagne, and G.G. Batrouni.

For any system of volume V, under external isotropic pressure P, the infinitesimal work done by the external forces is

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

then, based on the above *de facto* “theorem”, we have

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

The Equation of State for external isotropic pressure P:

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

applies to any material system.

- For crystals, Z and V are the partition function and the volume of an inner cell of the crystal, respectively.
- For non-crystals, Z and V are the partition function and the volume of the entire system, respectively.
- This equation is shown in every related (text)book.

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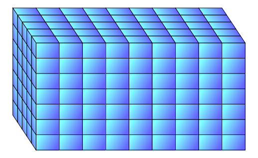
Summary

Now let us consider a crystal

made of the same cells tidily, concisely, and infinitely:



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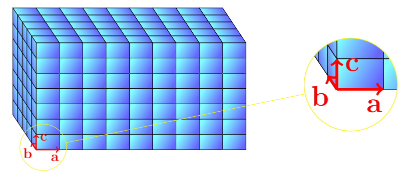
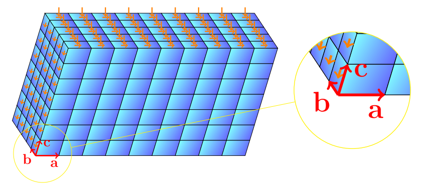


Let us call the red cell edge vectors $\mathbf{a}, \mathbf{b},$ and $\mathbf{c}$ as the period vectors to reflect the periodicity of the crystal structure.

A crystal may experience anisotropic external forces

The general external mechanical environment can be described by a symmetric stress $\mathbf{S}$ (a 3×3 matrix). The force on an area vector σ of a surface, by the stress, is $\mathbf{S} \cdot \sigma$.



Since the external forces on the crystal surfaces may be in any direction, with components parallel and/or perpendicular to the surfaces, the crystal may deform, and the period vectors $\mathbf{a}, \mathbf{b},$ and $\mathbf{c}$ change correspondingly and independently with each other.

For a crystal under general external stress $\mathbf{S}$

the previous Equation of State

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

for the isotropic external pressure P, can not apply.

For a crystal under general external stress $\mathbf{S}$,

Using $\sigma_{\mathbf{a}} = \mathbf{b} \times \mathbf{c}$, $\sigma_{\mathbf{b}} = \mathbf{c} \times \mathbf{a}$, and $\sigma_{\mathbf{c}} = \mathbf{a} \times \mathbf{b}$ as surface area vectors of a cell in the crystal, $\mathbf{S} \cdot \sigma_{\mathbf{a}}$, $\mathbf{S} \cdot \sigma_{\mathbf{b}}$, and $\mathbf{S} \cdot \sigma_{\mathbf{c}}$ are the equivalent external forces acting on the surfaces accordingly.

Then,

$$\mathrm{d}W = (\mathbf{S} \cdot \sigma_{\mathbf{a}}) \cdot \mathrm{d}\mathbf{a} + (\mathbf{S} \cdot \sigma_{\mathbf{b}}) \cdot \mathrm{d}\mathbf{b} + (\mathbf{S} \cdot \sigma_{\mathbf{c}}) \cdot \mathrm{d}\mathbf{c},$$

is the infinitesimal work done on the cell/crystal by the external stress.

For a crystal under general external stress $\mathbf{S}$,

the infinitesimal work done by the external forces is:

$$\mathrm{d}W = (\mathbf{S}\cdot\sigma_{\mathbf{a}})\cdot\mathrm{d}\mathbf{a} + (\mathbf{S}\cdot\sigma_{\mathbf{b}})\cdot\mathrm{d}\mathbf{b} + (\mathbf{S}\cdot\sigma_{\mathbf{c}})\cdot\mathrm{d}\mathbf{c}.$$

Then, based on the above *de facto* “theorem ”, we have

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

The *de facto* “theorem” in statistical physics

If the infinitesimal work done by the **EXTERNAL** forces on the system in a macroscopic equilibrium state is written in the form of

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

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

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

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

For a crystal, the derived equation: $\mathbf{S} \cdot \sigma_{\mathbf{h}} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c})$

determines the crystal period vectors $\mathbf{a}, \mathbf{b},$ and $\mathbf{c}$,

which determine the volume of the cell,

further determine the volume of the crystal,

then is the Equation of State for crystals under general external stress and temperature.

In 2010, in the book "Statistical Mechanics: Theory and Molecular Simulation", Tuckerman introduced the macroscopic internal stress $\mathbf{P}^{(\mathrm{int})}$ of crystals as Equation (5.6.9) (Equation (5.7.9) in the 2023 version):

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

Bringing it into $\mathbf{S} \cdot \sigma_{\mathbf{h}} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c})$, we get

$$\mathbf{S} \cdot \sigma_{\mathbf{h}} = -\mathbf{P}^{(\mathrm{int})} \cdot \sigma_{\mathbf{h}}, \quad \text{or} \ , \quad \mathbf{S} + \mathbf{P}^{(\mathrm{int})} = 0 \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}).$$

This is the Macroscopic Mechanical Equilibrium Condition:

the macroscopic internal stress balances the external stress.

For the special case of isotropic external pressure P, the stress becomes $\mathbf{S} = -P\mathbf{I}$, with $\mathbf{I}$ being the identity tensor.

The equation of state of crystals: $\mathbf{S} \cdot \sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c})$ becomes

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

which can be further written as: $PV = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{h}}\right) \cdot \mathbf{h} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}).$

Since isotropic, we may assume the crystal cell expands uniformly: all the directions of the period vectors are fixed and their magnitudes are proportional to $V^{1/3}$:

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

Then the equation of state of crystals: $\mathbf{S} \cdot \sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c})$

can reproduce the equation of state for isotropic external pressure:

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

The equation of state of crystals: $\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c})$

actually, was derived in our previous article:

“A new equation for period vectors of crystals under external stress and temperature in statistical physics: mechanical equilibrium condition and equation of state.”
Eur. Phys. J. Plus **136**, 48 (2021).
https://doi.org/10.1140/epjp/s13360-020-01010-6
(downloaded more than 24,000 times up to now.)

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Summary

Since the basic physical properties of a non-crystal system are intrinsic, they should not depend on their macroscopic shape. Then, the system may be chosen as only one but huge crystal “cell”, without periodicity in structures, and the “period vectors” are now only the edge vectors of the “cell”, but we may still call them the period vectors and use all the same symbols as previously.

Then the previous infinitesimal work done by the external stress $\mathbf{S}$ for crystals:

$$\mathrm{d}W = (\mathbf{S}\cdot\sigma_{\mathbf{a}})\cdot\mathrm{d}\mathbf{a} + (\mathbf{S}\cdot\sigma_{\mathbf{b}})\cdot\mathrm{d}\mathbf{b} + (\mathbf{S}\cdot\sigma_{\mathbf{c}})\cdot\mathrm{d}\mathbf{c},$$

also applies for non-crystals under external stress S.

As a result, based on the *de facto* “theorem”, the equation of state of crystals:

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

also applies for non-crystals under external stress S.

The equation:

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

also means the Macroscopic Mechanical Equilibrium Condition for non-crystals:
the macroscopic internal stress balances the external stress,
assuming that Tuckerman's internal stress $\mathbf{P}^{(\mathrm{int})}$ still applies.

In classical physics, the partition function Z can be factorized as $Z_k Z_u$:

$$\begin{aligned} Z_k &= \frac{V^N}{N!}\int\int\cdots\int\frac{1}{h^{3N}}e^{-\beta E_k(\mathbf{p})}\mathrm{d}\mathbf{p}_1,\mathrm{d}\mathbf{p}_2,\cdots,\mathrm{d}\mathbf{p}_N \\ Z_u &= \frac{1}{V^N}\int_V\int_V\cdots\int_V e^{-\beta E_p(\mathbf{R})}\mathrm{d}\mathbf{r}_1,\mathrm{d}\mathbf{r}_2,\cdots,\mathrm{d}\mathbf{r}_N. \end{aligned}$$

Then, $\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial\ln Z}{\partial\mathbf{h}} = -\frac{1}{\beta}\frac{\partial\ln Z_k}{\partial\mathbf{h}} - \frac{1}{\beta}\frac{\partial\ln Z_u}{\partial\mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c})$

can be expanded in every detail and shown that the averaged internal force and the external force balance each other explicitly.

Still for non-crystals, the equation:

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

can also reproduce the equation of state for isotropic external pressure.

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Concluding remarks: $\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\dfrac{1}{\beta}\dfrac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c})$

is derived based on the *de facto* “theorem”;
can serve as the Equation of State for all matters
under any external mechanical and thermal conditions;
then, may be applied to quasi-equilibrium thermodynamic processes.

All details of this talk are available in the preprint:

https://doi.org/10.20944/preprints202601.0293.v3

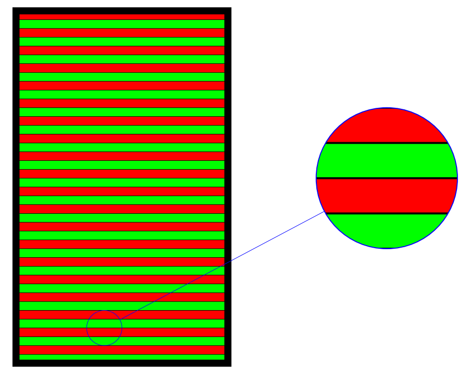
Many thanks for your attention and questions!

Discussion 01

If the earth gravity is considered, we may imagine that the system is cut into many horizontal layers, then apply

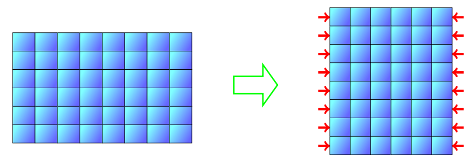
$$\mathbf{S} \cdot \sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}),$$

to each layer. Suppose every layer is thin enough, so that the gravity in it can be neglected, while the weight of other layers on it is still applied.



Discussion 02

As shown in the right figure, if additional external forces are applied to the left and right surfaces of a crystal (the red arrows), the cells may be caused to rearrange, for example, from 6×8 to 8×6 cells. This may be one way for the crystal to deform. Anyhow, the equation



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

still applies to every cell.