The Macroscopic Mechanical Equilibrium Condition Governing and Supporting Equilibrium States: the Physical Origin of the Equation of State

Gang Liu

gl.cell@outlook.com
https://orcid.org/0000-0003-1575-9290
http://www.linkedin.com/in/liuganglinkedin
Independent Researcher, Kingston, Ontario, Canada

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Fundamentals of the Equation of State

Forces Associated with Transport of Momentum

The Macroscopic Mechanical Equilibrium Condition

The Equation of State of Crystals

The Physical Origin of the Equation of State

Quasi-Equilibrium Thermodynamic Processes and Examples

Calculation Examples

Generalization of the Equation of State

Summary

The Equation of State (EOS)

- was studied/published as early as in the mid 17th century:
  - https://en.wikipedia.org/wiki/Boyle%27s_law (1662: $P_1 V_1 = P_2 V_2$),
  - https://en.wikipedia.org/wiki/Equation_of_state .
- As a comparison, the great book *Philosophiæ Naturalis Principia Mathematica* by Newton was published in 1687:
  - https://en.wikipedia.org/wiki/Philosophi%C3%A6_Naturalis_Principia_Mathematica.

What is the EOS?

- A simple answer: an equation to determine the **volume** of a fixed amount of matter under an arbitrarily given external **pressure and temperature**.

The EOS yields the fixed volume of a certain amount of matter under given external conditions.

- For a given system, if the volumes are the same in both an equilibrium and non-equilibrium states, the EOS can be said for the equilibrium state.
- For the same system, if the volumes are different between the equilibrium and non-equilibrium states, the EOS can only be said for the equilibrium state.
- In one word, the EOS is meaningful only for materials in a macroscopic equilibrium state, because the EOS only gives us the fixed and unique volume, under given external conditions.

Then what is the physics behind the EOS?

Since the EOS is only for macroscopic equilibrium states

- the macroscopic thermal and mechanical equilibrium conditions apply.
- The macroscopic thermal equilibrium condition is satisfied, as long as the temperature inside the system everywhere is assumed the same as the fixed external temperature.
- Meanwhile, we may focus on the macroscopic mechanical equilibrium condition (MMEC).

Let us imagine to cut a material system in a macroscopic equilibrium state into a great number of small, yet macroscopic pieces, with pure static geometric planes.

- Then the macroscopic equilibrium state and the MMEC hold for each piece.
- The macroscopic internal stress at every macroscopic point of the system balances the external stress applied onto the system.
- Determining the equilibrium positions of all the inside microscopic particles, the MMEC determines the actual unique volume of the system under given external temperature and mechanical condition.
- Now supposing we get a rigorous EOS by any means, it must yield the same volume of the system as that generated by the MMEC.
- As the MMEC is essentially an established physics principle, it can be regarded as the physical origin/foundation of the EOS.

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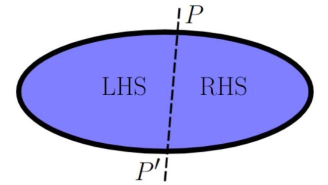
While the system is in a macroscopic equilibrium state,
the microscopic particles inside, running as thermal motions
and experiencing all kinds of forces constantly,
may not be in an equilibrium state.

Lut us imagine to cut an Ideal Gas

- with a static pure geometric plane PP' into approximately two halves:



- Then explicitly define the Right Half System (RHS) only based on the space enclosed by the plane PP' and the contacted part of the inner walls of the container containing the ideal gas. This means that at any given time only microscopic particles inside this space and all such particles belong to the RHS.
- As a result, the RHS is statistically in a macroscopic equilibrium state.
- The Left Half System (LHS) is defined the same way.

Assuming no collision in the plane PP'

- When a particle crosses the plane PP' from the RHS into the LHS, the RHS loses momentum, roughly speaking, in the left direction. This means that the RHS gets momentum in the right direction.

- On the other hand, when a particle crosses the plane PP' from the LHS into the RHS, the RHS gets momentum in the right direction straightforwardly.

- So, for all particles running between the RHS and LHS, the RHS always acquires momentum in the right direction. Let us define the time rate of the momentum change as the force associated with transport of momentum, as we did previously: https://doi.org/10.1139/cjp-2014-0518 , though no actual regular force here.

Still working on the Ideal Gas

- The pressure of the force associated with transport of momentum can be derived based on statistics as
$$\frac{1}{V}nRT,$$
where V is the volume of the gas, n is the amount of the gas (in moles), $R = 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is the universal gas constant, and T is the absolute temperature.
- The above pressure between the RHS and the LHS is the internal pressure of the ideal gas.
- If we apply the mechanical equilibrium condition: the external pressure P balances the above internal pressure, we can get the EOS of the ideal gas
$$PV = nRT.$$

Still for the Ideal Gas

- In another extreme case, whenever a particle from one side runs into the plane PP', another particle from the other side runs to the same spot, then they collide and both are bounced back to their original side respectively.
- Here the force associated with transport of momentum is zero.
- However, the concrete forces in all the collisions are there now. The pressure of the total collision forces can also be derived based on statistics as

$$\frac{1}{V}nRT.$$

Still for the Ideal Gas

- If some particles collide in the plane PP', and all others run through the plane PP', the total pressure of the force associated with transport of momentum and the collision forces should remain the same as
$$\frac{1}{V}nRT,$$
regardless of how many collisions happening.
- In fact, a collision can be regarded as an event that one particle runs from the RHS into the the LHS and another particle deos the opposite, with no interaction.

Last View for the Ideal Gas

- Considering statistics of the ideal gas in a macroscopic equilibrium state, the velocity of a particle can be assumed with the same possibility in all directions with the same magnitude. And it can appear anywhere in the system with the same possibility as well.
- This means whenever a particle runs into the plane PP' with a certain velocity from the RHS, its "reflected" one running back into the RHS from the plane can always be assumed at the same time.
- As this action is done by the LSH, the LSH can be equivalently regarded as a wall to the RHS. Then the pressure of the action is still

$$\frac{1}{V}nRT.$$

A quick summary for the Ideal Gas

- In all the above situations, the internal pressure is derived the same as

$$\frac{1}{V}nRT,$$

- By applying the mechanical equilibrium condition, we get

$$PV = nRT,$$

  which is the EOS of the ideal gas.

- In all the derivation, the force associated with transport of momentum is employed as a regular force whenever applicable.

- Outline: 1

The Thermal Pressure

- All the previous mechanical equilibrium conditions are actually based on the Newton's Second Law.
- Also in those conditions, the force associated with transport of momentum, representing the momentum change due to the border crossing of microscopic particles, are employed as a regular force whenever applicable.
- Describing thermal motion effects, the force associated with transport of momentum can be assumed in all material systems.
- With the aid of statistics, the pressure of the force associated with transport of momentum of a macroscopic equilibrium system can be derived as

  $$\frac{1}{V}nRT.$$

  Let us call it as the thermal pressure.

The Macroscopic Mechanical Equilibrium Condition (MMEC)

- Let us further call
  the total of
  the thermal pressure
  and
  the pressure/stress of all other internal forces
  as the macroscopic internal pressure/stress.
- Then, the MMEC means that
  the macroscopic internal stress and the external stress balances each other.

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Summary

Periodic Systems: Crystals

- A crystal is made of a three-dimensional periodic arrangement of exactly the same cells.
- Each cell, containing the same microscopic particles, is a parallelepiped.
- Since a crystal is essentially an unlimited periodic structure, let us call the edge vectors of the parallelepiped cell as the (crystal) period vectors.

Crystal Structure

- The positions of all microscopic 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?

The EOS for crystals under an isotropic pressure

- is for the situation where the external pressure acting on the crystal is the same (unique) from all directions.
- The rigorous theoretical EOS is presented in almost all related books, with the assumption that the cell shape is known and does not change:

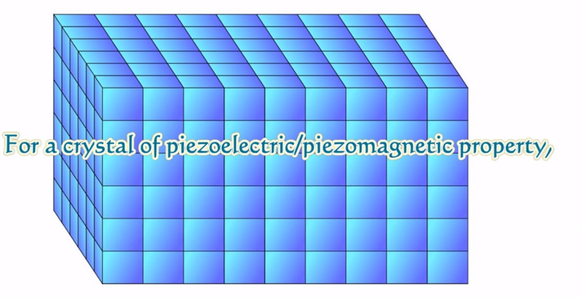
  $$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}, \tag{7}$$

  where $\beta = 1/(kT)$, and k, Z, and V are the Boltzmann constant, the partition function of the system, and the cell volume, respectively.
- However, there are situations where the external pressure is not the same in all directions. The cell shape may also change or may not even be known beforehand.

The Piezoelectricity and Piezomagnetism

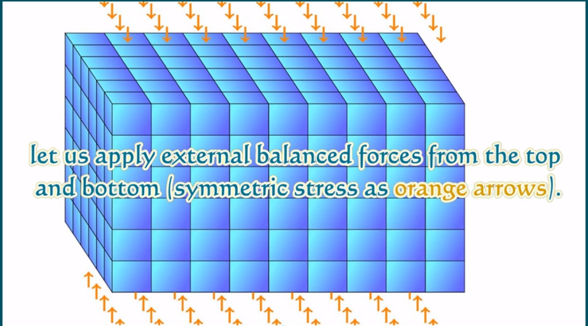
- are so fascinating that electric or magnetic field may be created by simply applying mechanical forces on certain crystals!
- For that purpose, be sure to apply an additional pressure on the crystal but only in one direction, while keeping the pressure perpendicular to it remain unchanged.

The Piezoelectricity and Piezomagnetism



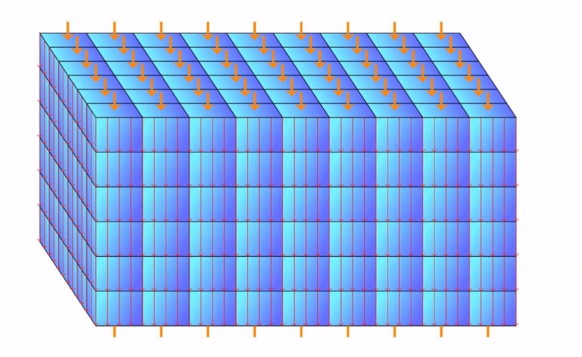
For a crystal of piezoelectric/piezomagnetic property,

The Piezoelectricity and Piezomagnetism

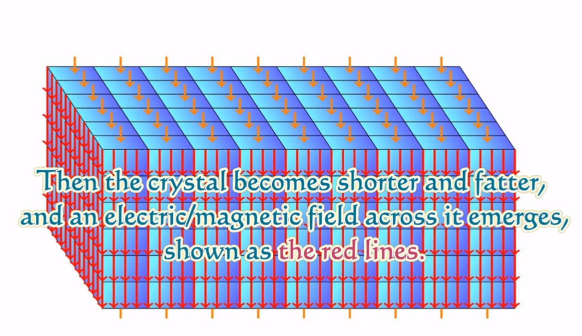


let us apply external balanced forces from the top and bottom (symmetric stress as orange arrows).

The Piezoelectricity and Piezomagnetism



The Piezoelectricity and Piezomagnetism



Then the crystal becomes shorter and fatter, and an electric/magnetic field across it emerges, shown as the red lines.

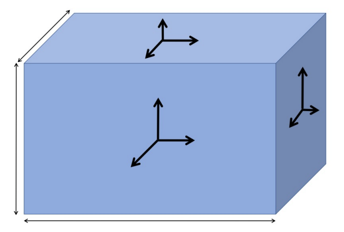
The Piezoelectricity and Piezomagnetism

- Here, the external pressure is not the same in all directions and the cell shape should also change.
- Therefore the EOS for unique pressure: $$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} \tag{7}$$

  cannot apply here, as it can accept only one pressure value.

Actually, Crystals

- may experience more complicated external forces that even include components parallel to the crystal surfaces.



- Such complicated external forces can be described by the so-called Stress.

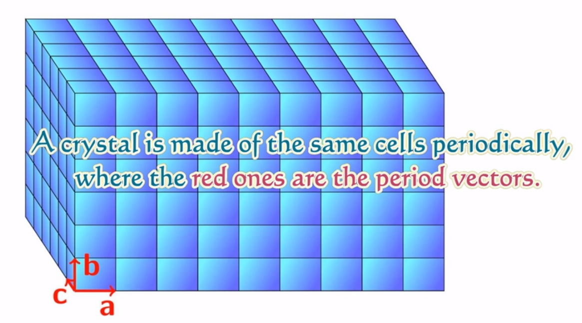
What is Stress?

- Let us recall pressure first: the normal force per unit area.
- Roughly speaking, stress is the total force acting on a surface per unit area vector.
- Stress is expressed as a second-rank tensor (3×3 matrix):

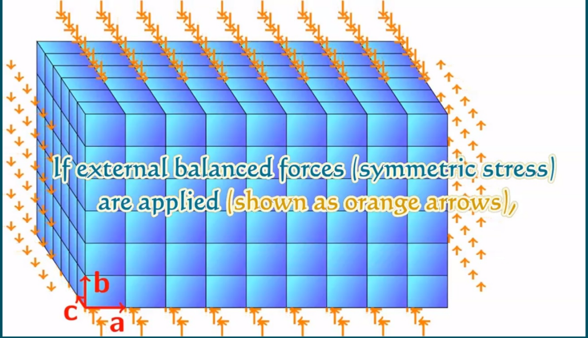
$$\mathbf{S} = \begin{pmatrix} S_{x,x} & S_{x,y} & S_{x,z} \\ S_{y,x} & S_{y,y} & S_{y,z} \\ S_{z,x} & S_{z,y} & S_{z,z} \end{pmatrix} .$$

- Then the force by the stress $\mathbf{S}$ acting on the area vector σ of a surface is $\mathbf{S} \cdot \sigma$.
- In order to keep a crystal in an equilibrium state, the external stress $\mathbf{S}$ must be symmetric: $S_{x,y} = S_{y,x}; \quad S_{x,z} = S_{z,x}; \quad S_{y,z} = S_{z,y}$.
- For the special case of the same pressure P in all directions, the stress reduces to: $\mathbf{S} = -P\mathbf{I}$, with $\mathbf{I}$ being an identity tensor.

Period Vectors under External Stress

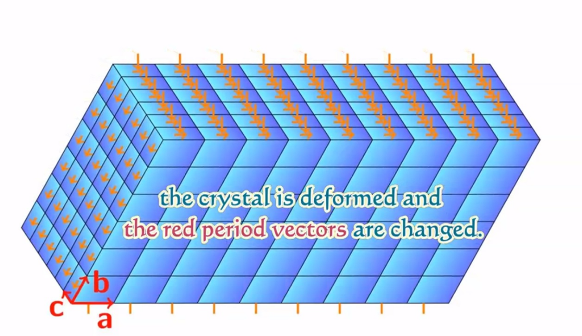


Period Vectors under External Stress



If external balanced forces (symmetric stress) are applied (shown as orange arrows),

Period Vectors under External Stress



the crystal is deformed and
the red period vectors are changed.

Crystal Period Vectors under External Stress

- As shown in a previous simulation, the crystal period vectors (cell edge vectors) may change independently according to the external stress $\mathbf{S}$ applied.
- The recent publication in *The European Physical Journal Plus* (EPJP):
  https://doi.org/10.1140/epjp/s13360-020-01010-6 (free for downloading)
  derived a new equation to determine the period vectors for crystals under arbitrary external stress and temperature, based on the principles of statistical physics.

Derivation of the Equation

- Let us first recall how the EOS for crystals under a unique pressure was derived.
- The first step was to express the work done by the external pressure equivalently on the crystal cell as

$$dW = -PdV.$$

- Then the EOS can be obtained immediately:

$$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}. \tag{7}$$

Please note in this presentation we use the same equation numbers from https://doi.org/10.1140/epjp/s13360-020-01010-6 .

Derivation of the Equation

- The following is a widely-used de facto "theorem" of Statistical Physics, derived from the first law of thermodynamics:
  If the work done by the external forces on a system is written in the form
  $$dW = A_1 dB_1 + A_2 dB_2 + \cdots + A_m dB_m,$$
  then for any pair of variables A_i and B_i, we have
  $$A_i = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial B_i} \quad (i = 1, 2, \cdots, m).$$
- See Eqns (2.95), (3.3), and (3.129) in the book *Equilibrium and Non-equilibrium Statistical Thermodynamics* by Bellac, Mortessagne, and Batrouni (Cambridge University Press, 2004).
- The above equation
  $$(dW = -PdV \ \Rightarrow) \quad P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}, \tag{7}$$
  was derived from this "theorem" for the isotropic external pressure.

Derivation of the Equation

- More specifically, the work expression by the isotropic external pressure

  $$dW = -PdV$$

  was based on the fact that the external forces act only on the surfaces of the crystal, then equivalently on the surfaces of the cell.
- We will do analogously for general external stress.

Derivation of the Equation

- For the crystal period vectors ($\mathbf{h} = \mathbf{a}$, or $\mathbf{b}$, or $\mathbf{c}$, forming a right-handed system), let us introduce the corresponding surface area vectors of the cell:

$$\sigma_{\mathbf{a}} = \mathbf{b} \times \mathbf{c}, \quad \sigma_{\mathbf{b}} = \mathbf{c} \times \mathbf{a}, \quad \sigma_{\mathbf{c}} = \mathbf{a} \times \mathbf{b}.$$

- Then as in https://doi.org/10.1140/epjp/s13360-020-01010-6 , the work done by the external stress $\mathbf{S}$ equivalently on the crystal cell can be derived as

$$dW = (\mathbf{S} \cdot \sigma_{\mathbf{a}}) \cdot d\mathbf{a} + (\mathbf{S} \cdot \sigma_{\mathbf{b}}) \cdot d\mathbf{b} + (\mathbf{S} \cdot \sigma_{\mathbf{c}}) \cdot d\mathbf{c}, \tag{1}$$

  where $\mathbf{S} \cdot \sigma_{\mathbf{h}}$ is the external force acting on the cell surface $\sigma_{\mathbf{h}}$, and $d\mathbf{h}$ is the displacement of that surface $(\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c})$.

- Based on the above "theorem" of Statistical Physics, the equation

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

  follows immediately.

The EOS for Crystals under External Stress

- The volume of the cell is determined by the crystal period vectors:

$$V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}.$$

- The equation that determines the crystal period vectors:

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

therefore is the EOS for crystals under arbitrary external stress and temperature.

Isotropic pressure: a special case

- For the special case of isotropic pressure P, where $\mathbf{S} = -P\mathbf{I}$, Equation (2)

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

- Meanwhile the crystal cell can be assumed expanded uniformly. That means all period vectors are fixed in direction and proportional to $V^{1/3}$ in length, then

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

- Then

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

Isotropic pressure: a special case

- Therefore

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

covers the special case of the external isotropic pressure:

$$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}. \tag{7}$$

- Even further relationships,

$$P = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)\frac{V}{V} = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{a}}\right)\cdot\frac{\mathbf{a}}{V} = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{b}}\right)\cdot\frac{\mathbf{b}}{V} = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \mathbf{c}}\right)\cdot\frac{\mathbf{c}}{V}.$$

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The Physical Origin of the EOS

- As we talked earlier in this presentation, the EOS is meaningful only for macroscopic matter in a macroscopic equilibrium state.
- Since in a macroscopic equilibrium state,

  the Macroscopic Mechanical Equilibrium Condition (MMEC) applies.
- From another point of view, once the independent period vectors and all positions of particles in a cell are known, everything about the crystal is determined, in other words these are the degrees of freedom of the crystal system.
- In principle, the positions of the particles in the cell may be obtained through Newtonian Mechanics or Quantum Mechanics, the period vectors (of total nine independent components) are the only degrees of freedom left.
- Conceptually, the MMEC (of total nine independent scalar equations) completely determines these period vectors.

The Physical Origin of the EOS

- Once all the degrees of freedom of the crystal are determined, no additional independent equation is needed or even permitted, governing the system.
- However, on the other hand, the EOS was rigorously derived. Since the EOS and the MMEC are both for determining the period vectors, they must be essentially the same.
- This shows again that the MMEC is the physical origin of the EOS but from the degree of freedom point of view for crystals, and also means that if the EOS is not satisfied, the system can not be in an equilibrium state.

The Physical Origin of the EOS

- Tuckerman introduced the (macroscopic) internal stress $\mathbf{P}^{(\mathrm{int})}$ for crystals in Equation (5.6.9) of his book *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, Oxford, 2010):

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

- Combining this with our EOS

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

yields

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

which reduces to

$$\mathbf{S} + \mathbf{P}^{(\mathrm{int})} = 0. \tag{12}$$

- So our EOS is the MMEC: the macroscopic internal stress balances the external stress.

Partition Function Z in the EOS

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

- is defined, in quantum physics, as

  $$Z = \sum_{s} e^{-\beta E_s},$$

  where the summation is over all energy levels E_s of the system. Straightforward but rather difficult to calculate in reality.

- Let us discuss some details in classical physics as follows.

Partition Function Z in Classical Physics

- can be factorized as

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

  where Z_k and Z_u are contributed from the particles' kinetic energy E_k and the cell potential energy E_p, respectively:

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

  where h is the Planck constant and N is the total number of particles in the cell. The integration is performed over all particle momenta $\mathbf{p}$ in Eq. (16), and over all particle positions $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N\}$ within the cell for Eq. (17).

Partition Function Z in Classical Physics

- Since the integration in

$$Z_k = \frac{V^N}{N!} \int \int \cdots \int \frac{1}{h^{3N}} e^{-\beta E_k(\mathbf{p})} d\mathbf{p}, \tag{16}$$

has nothing to do with the period vectors, the derivative is straightforward:

$$-\frac{1}{\beta}\frac{\partial \ln Z_k}{\partial \mathbf{h}} = -\frac{1}{\beta}\frac{N}{V}\frac{\partial V}{\partial \mathbf{h}} = -\frac{1}{V} NkT\sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{18}$$

Partition Function Z in Classical Physics

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

$$\mathbf{r}_i = r_{i,\mathbf{a}}\mathbf{a} + r_{i,\mathbf{b}}\mathbf{b} + r_{i,\mathbf{c}}\mathbf{c} \quad (i = 1, \cdots, N), \tag{19}$$

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

$$r_{i,\mathbf{h}} = \frac{1}{V}\mathbf{r}_i \cdot \sigma_{\mathbf{h}} \qquad (i = 1, \cdots, N;\ \mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{20}$$

- Then the following original integration over $\mathbf{r}_i$ in the whole cell volume can be converted into that over the scaled coordinates from 0s to 1s:

$$\frac{1}{V}\int_V \cdots d\mathbf{r}_i \;\;=\;\; \int_V \cdots \frac{d\mathbf{r}_i}{V} = \int_0^1\int_0^1\int_0^1 \cdots dr_{i,\mathbf{a}}dr_{i,\mathbf{b}}dr_{i,\mathbf{c}} \quad (i = 1, \cdots, N).$$

Partition Function Z in Classical Physics

- Since $$\frac{1}{V}\int_V \cdots d\mathbf{r}_i = \int_0^1\int_0^1\int_0^1 \cdots dr_{i,\mathbf{a}}dr_{i,\mathbf{b}}dr_{i,\mathbf{c}} \quad (i = 1, \cdots, N),$$

  we have
  $$\begin{aligned}\frac{\partial Z_u}{\partial \mathbf{h}} &= \frac{\partial}{\partial \mathbf{h}}\left(\frac{1}{V^N}\int_V\int_V\cdots\int_V e^{-\beta E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}d\mathbf{R}\right)\\ &= \int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\int_0^1\cdots\int_0^1\int_0^1\int_0^1 \frac{\partial}{\partial \mathbf{h}}e^{-\beta E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})} \times \\ &\qquad dr_{1,\mathbf{a}}dr_{1,\mathbf{b}}dr_{1,\mathbf{c}}dr_{2,\mathbf{a}}dr_{2,\mathbf{b}}dr_{2,\mathbf{c}}\cdots dr_{N,\mathbf{a}}dr_{N,\mathbf{b}}dr_{N,\mathbf{c}}\\ &\qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}).\end{aligned} \tag{22}$$

Partition Function Z in Classical Physics

- Further considering the dependency of $\mathbf{R}$ on the period vectors,

$$\frac{\partial E_p}{\partial \mathbf{h}} = \left.\frac{\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}{\partial \mathbf{h}}\right|_{\mathbf{R}} + \left.\frac{\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}{\partial \mathbf{h}}\right|_{\mathbf{a},\mathbf{b},\mathbf{c}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \qquad (23)$$

-

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

where $\mathbf{F}_i = -\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})/\partial \mathbf{r}_i$ is the net force acting on particle i.

Partition Function Z in Classical Physics

- In the integration with respect to $\mathbf{R}$ in Equation (27)

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

  the minimum $E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})$ means the most probable state.
- It corresponds to that

$$
\mathbf{F}_i = -\frac{\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}{\partial \mathbf{r}_i} = 0, \quad (i = 1, 2, \cdots, N).
$$

Partition Function Z in Classical Physics

- Further considering that other states may cancel each other, let us only consider the most probable state, then Equation (27) becomes

$$-\frac{\partial \ln Z_u}{\beta \partial \mathbf{h}} = \left.\frac{\partial E_p(\mathbf{a},\mathbf{b},\mathbf{c},\mathbf{R})}{\partial \mathbf{h}}\right|_{\mathbf{R}} - \frac{1}{V}\sum_{i=1}^{N} \mathbf{F}_i \otimes \mathbf{r}_i \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}).$$

- Equation (2) becomes

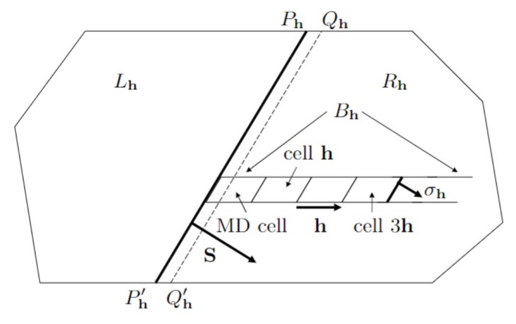
$$\begin{aligned}\mathbf{S}\cdot\sigma_{\mathbf{h}} &= -\frac{1}{\beta}\frac{\partial \ln Z_k}{\partial \mathbf{h}} - \frac{1}{\beta}\frac{\partial \ln Z_u}{\partial \mathbf{h}} \\ &= -\frac{1}{V}NkT\sigma_{\mathbf{h}} + \left.\frac{\partial E_p}{\partial \mathbf{h}}\right|_{\mathbf{R}} - \frac{1}{V}\sum_{i=1}^{N} \mathbf{F}_i \otimes \mathbf{r}_i \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}). \quad (51)\end{aligned}$$

Molecular Dynamics Simulation

- is a very active research field that is closely related to the EOS. It usually applies Newtonian Dynamics throughout.
- It is common to apply the periodic boundary condition, i.e. to describe the system as if it were a periodic structure. The corresponding period vectors need to be dynamically simulated/determined. Much effort has been made to derive such dynamics.

Molecular Dynamics Simulation

- For that purpose, the paper https://dx.doi.org/10.1139/cjp-2014-0518 “cuts” the periodic system into a left part $L_\mathbf{h}$ and a right part $R_\mathbf{h}$ with respect to a period vector $\mathbf{h}$:



- Then applies the Newton’s Second Law on the right part.

Molecular Dynamics Simulation

- As a result, the dynamical equation for the period vectors was acquired:

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

  with the internal stress

  $$\pi = \frac{1}{3V}\sum_{i=1}^{N} m_i \left|\dot{\mathbf{r}}_i\right|^2 \mathbf{I} - \frac{1}{V}\sum_{\mathbf{z}\in\text{DOF}} \left(\frac{\partial E_p}{\partial \mathbf{z}}\right) \otimes \mathbf{z},$$

  where $\alpha_{\mathbf{h},\mathbf{h}}$ is an effective mass, N is the total number of particles in a cell, m_i is the mass of particle i, $\mathbf{r}_i$ is its position vector, DOF refers to all degrees of freedom of the system, and E_p is the total potential energy of a cell.

- And for all particles in the cell, the rigorous Newton's Second Law still applies:

  $$m_i\ddot{\mathbf{r}}_i = \mathbf{F}_i \quad (i = 1, 2, \cdots, N),$$

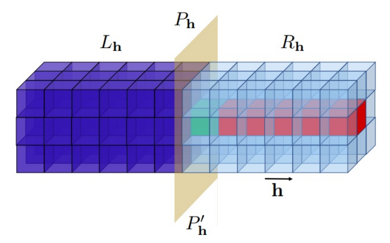
  where $\mathbf{F}_i$ is the net force on particle i from all other particles in any cell.

Molecular Dynamics Simulation

- If we set all accelerations to zero, the dynamical equation of the period vectors
$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = (\pi + \mathbf{S}) \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}),$$
becomes the Newtonian Dynamical form of the EOS of the system, and is also the MMEC in classical physics:
$$\pi + \mathbf{S} = 0,$$
with the internal stress
$$\pi = \frac{1}{3V}\sum_{i=1}^{N} m_i \left|\dot{\mathbf{r}}_i\right|^2 \mathbf{I} - \frac{1}{V}\sum_{\mathbf{z}\in\text{DOF}} \left(\frac{\partial E_p}{\partial \mathbf{z}}\right) \otimes \mathbf{z}.$$
- The last two equations are equivalent to Equation (51) (Equation (2)):
$$\mathbf{S} \cdot \sigma_{\mathbf{h}} \quad = \quad -\frac{1}{V}NkT\sigma_{\mathbf{h}} + \left.\frac{\partial E_p}{\partial \mathbf{h}}\right|_{\mathbf{R}} - \frac{1}{V}\sum_{i=1}^{N} \mathbf{F}_i \otimes \mathbf{r}_i \cdot \sigma_{\mathbf{h}} \qquad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}). \quad (51)$$
- So again the EOS of Equation (2) is the MMEC.

Molecular Dynamics Simulation

- In the above internal stress and Equation (51), the term: $-\left.\dfrac{\partial E_p}{\partial \mathbf{h}}\right|_{\mathbf{R}}$
  is the net regular force, by the left half crystal (blue cells), on the green and red cells, constituting a half-unlimited bar, (excluding the thermal pressure,) shown below:



- This was shown in https://dx.doi.org/10.1139/cjp-2014-0518 for pair potential and
- Many-body interactions: https://www.preprints.org/manuscript/201709.0030/v2

- Outline: 1

The Physical Meaning of the EOS

- Let us suppose that the macroscopic shape and volume of a given crystal are determined by the crystal period vectors (proportionally).
- Our EOS
$$\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}), \tag{2}$$
determines the period vectors then the geometry of the crystal under external stress and temperature.
- It therefore describes the thermodynamic quasi-equilibrium processes of the crystal, including expansions due to external forces and/or temperature. The corresponding coefficients and constants may also be calculated theoretically.

Thermodynamic Quasi-Equilibrium Processes

- If external stress and/or temperature causes the period vectors to change from $\mathbf{a}_i$, $\mathbf{b}_i$, $\mathbf{c}_i$, to $\mathbf{a}_f$, $\mathbf{b}_f$, $\mathbf{c}_f$, the work done by the external stress on the cell may be expressed as

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

- This follows from the relation presented earlier:

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

- The total heat that needs to be supplied to the crystal in this process is

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

where the initial and final internal energies are $E_{t,i}$ and $E_{t,f}$, repsectively.

Piezoelectric/Piezomagnetic Processes

- When an additional pressure is applied along a specific direction, the crystal period vectors change.
- The EOS:

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

  can be used to calculate these vectors and therefore the new crystal structure.
- Since the new electric/magnetic field should be created by the new structure of the crystal, this EOS may help studying these phenomena.

Constant Temperature

- The EOS
$$\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}), \tag{2}$$
may be used to calculate the crystal period vectors for a given external stress.
- When the external stress changes later, we can re-calculate the period vectors.
- If the change in the period vectors is proportional to the change of the external stress, we are observing the process by the (Generalized) Hooke's Law.
- Since both changes of the period vectors and the external stress are available in theory now, the elastic constants for the law can be calculated.

- Outline: 1

Fundamentals of the Equation of State

Forces Associated with Transport of Momentum

The Macroscopic Mechanical Equilibrium Condition

The Equation of State of Crystals

The Physical Origin of the Equation of State

Quasi-Equilibrium Thermodynamic Processes and Examples

Calculation Examples

Generalization of the Equation of State

Summary

In 2010, Ma and Tuckerman applied the Quantum Mechanical Form of the EOS to the study of a silicon crystal under isotropic pressure:

https://doi.org/10.1063/1.3499812

Demonstration

https://doi.org/10.1140/epjp/s13360-020-01010-6 employed the Newtonian Dynamical form of the EOS to the study of thermodynamic quasi-equilibrium processes in a one-dimensional "crystal":

- Compression/expansion by external forces at constant temperature, elastic constants for Hooke's law, and the crystal breaking point were calculated.
- Heating from external temperature at constant external forces and crystal melting point were calculated.
- The breaking and melting points were determined based on that the MMEC cannot be satisfied beyond them.

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The equation: $$\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}) \tag{2}$$
applies to periodic systems.

- Any limited real gas, liquid, or non-crystal solid may experience external forces on their surfaces.
- In such a situation, the microscopic particles at the boundaries experience the external forces directly, while the interior particles not. Then they should be treated differently in the dynamics and the partition function.
- This may impose further difficulties in the calculation.

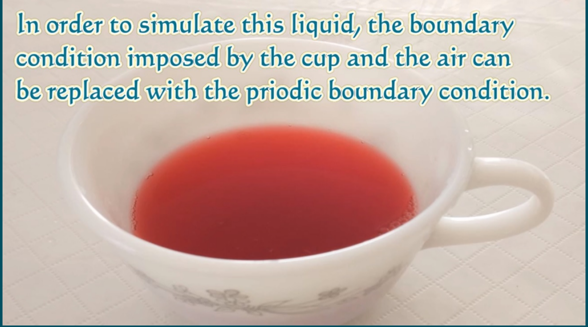
The equation: $$\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}) \tag{2}$$
applies to periodic systems.

- To solve the above problem, the periodic boundary conditions are often used.
- Then the system gets a complete periodic structure, and becomes a crystal.

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

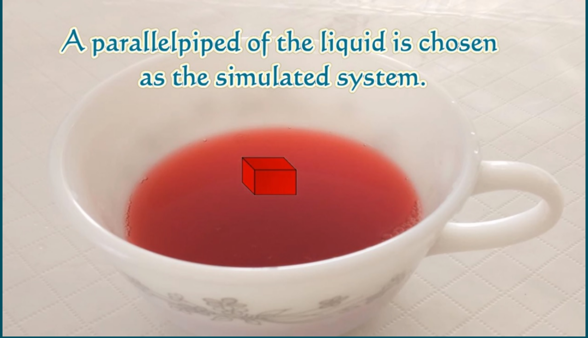
applies to periodic systems.

The equation: $$\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}) \tag{2}$$ applies to periodic systems.

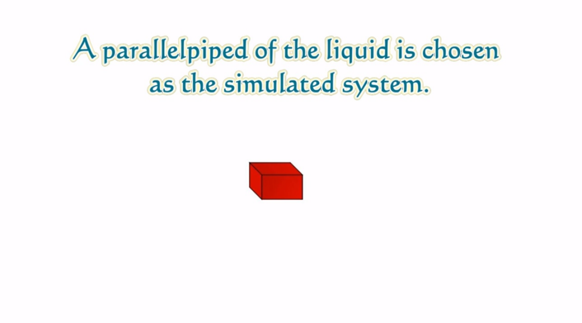

In order to simulate this liquid, the boundary condition imposed by the cup and the air can be replaced with the priodic boundary condition.

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

applies to periodic systems.

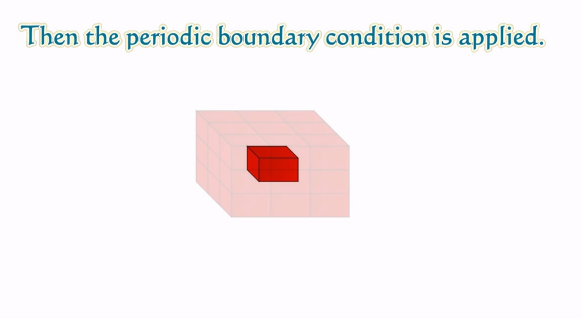


The equation: $$\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}) \tag{2}$$ applies to periodic systems.



A parallelpiped of the liquid is chosen as the simulated system.

The equation: $$\mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}) \tag{2}$$
applies to periodic systems.


Then the periodic boundary condition is applied.

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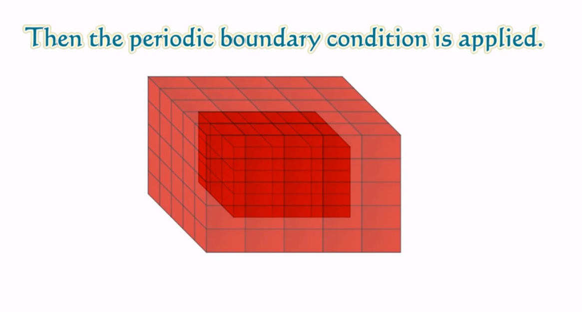

Then the periodic boundary condition is applied.

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

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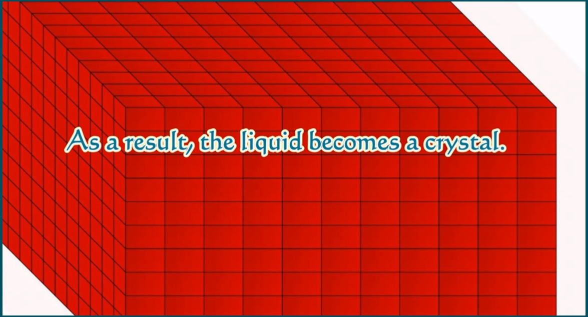

The equation: $$\mathbf{S} \cdot \sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}) \tag{2}$$

applies to periodic systems.

- To solve the above problem, the periodic boundary conditions are often used.
- Then the system gets a complete periodic structure, and becomes a crystal.
- More importantly, the real external forces on the original surfaces are equivalently replaced with the forces from the new imagined surrounding cells. So all microscopic particles are now in the same environment and can be treated the same way in dynamics and partition function.
- Under these circumstances, equation (2) and all conclusions based on it apply.

$$\text{Both equations}\quad \mathbf{S}\cdot\sigma_{\mathbf{h}} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathbf{h}} \quad (\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}) \quad \text{and} \tag{2}$$

$$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}, \tag{7}$$

apply to periodic systems or systems with periodic boundary conditions applied, under the isotropic pressure.

- However, the former has nine coupled scalar equations, while the latter is only one.
- The latter is actually a linear combination of the former scalar equations.
- So the former is more detailed than the latter and implies the latter.

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

- was derived exactly the same way as the widely-accepted and extensively-used equation $P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$ was derived for the isotropic external pressure;
- covers the isotropic external pressure as a special case;
- can be converted into the specific form of the MMEC: $\mathbf{S} + \mathbf{P}^{(\mathrm{int})} = 0$, with Tuckerman's macroscopic internal stress $\mathbf{P}^{(\mathrm{int})} = \frac{1}{\beta V}\sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}} \frac{\partial \ln Z}{\partial \mathbf{h}} \otimes \mathbf{h}$;
- can reproduce the MMEC: $\mathbf{S} + \frac{1}{3V}\sum_{i=1}^{n} m_i \left|\dot{\mathbf{r}}_i\right|^2 \mathbf{I} - \frac{1}{V}\sum_{\mathbf{z}\in\mathsf{DOF}} \left(\frac{\partial E_p}{\partial \mathbf{z}}\right) \otimes \mathbf{z} = 0$ achieved earlier based on the pure Newtonian Dynamics;
- governs and supports the equilibrium states, is the MMEC, and is the EOS of material systems as well.

References and Supporting Materials

1	M.E. Tuckerman: *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, Oxford, 2010)
2	Z. Ma, M.E. Tuckerman: https://doi.org/10.1063/1.3499812
3	M.L. Bellac, F. Mortessagne, G.G. Batrouni: *Equilibrium and Non-Equilibrium Statistical Thermodynamics* (Cambridge University Press, Cambridge, 2004)
4	Gang Liu, http://dx.doi.org/10.1139/cjp-2014-0518
5	Gang Liu, https://www.preprints.org/manuscript/201709.0030/v2
6	Gang Liu: https://doi.org/10.1140/epjp/s13360-020-01010-6
7	https://1drv.ms/f/s!Ap9xNuiPY91U1mfryMqyo7iUENXC?e=mKmnJh

Thank you very much for your attention!