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

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- Outline: 1

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- 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?

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- 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.

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- 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?

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- Meanwhile, we may focus on the macroscopic mechanical equilibrium condition (MMEC).

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- 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, 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.

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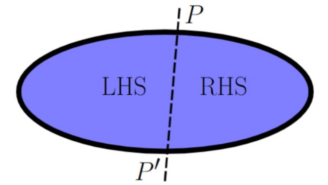
- with a static pure geometric plane PP' into approximately two halves:



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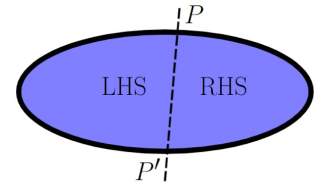

- Then explicitly define the Right Half System (RHS) only based on the space enclosed by the plane PP' and the contacted part of the inner walls of the container containing the ideal gas. This means that at any given time only microscopic particles inside this space and all such particles belong to the RHS.

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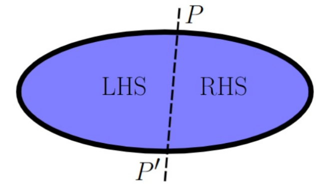

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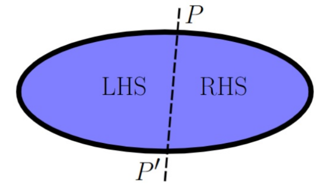

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- As a result, the RHS is statistically in a macroscopic equilibrium state.
- The Left Half System (LHS) is defined the same way.

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- 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.

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- 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
$$PV = nRT.$$

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- 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

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- 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

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- 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.

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- 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.

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- 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

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- By applying the mechanical equilibrium condition, we get

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  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.

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- 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

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  Let us call it as the thermal pressure.

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  the macroscopic internal stress and the external stress balances each other.

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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

Periodic Systems: Crystals

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- 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.

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- 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?

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

  where $\beta = 1/(kT)$, and k, Z, and V are the Boltzmann constant, the partition function of the system, and the cell volume, respectively.

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  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.

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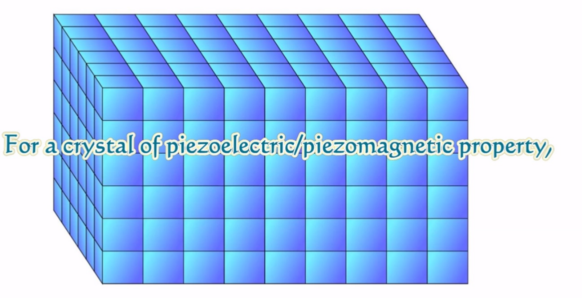
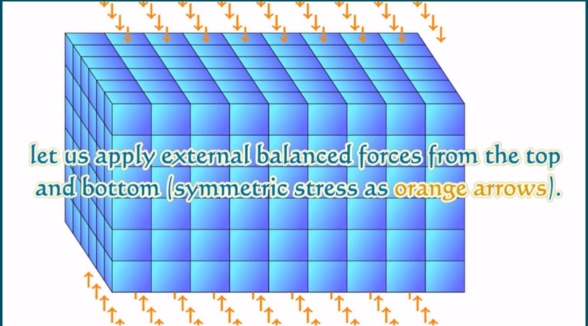
- are so fascinating that electric or magnetic field may be created by simply applying mechanical forces on certain crystals!
- For that purpose, be sure to apply an additional pressure on the crystal but only in one direction, while keeping the pressure perpendicular to it remain unchanged.

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).

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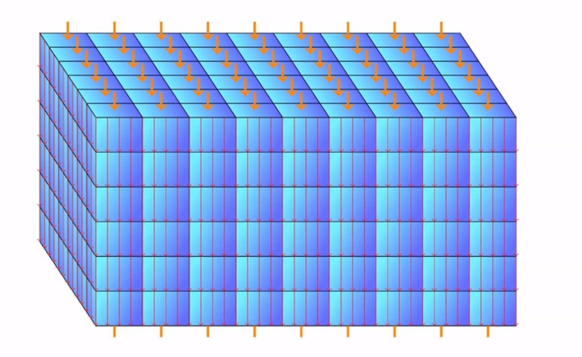

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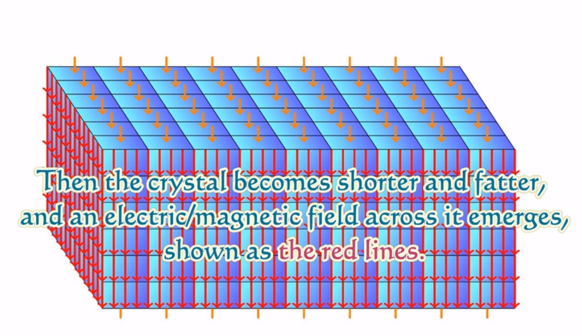

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- Therefore the EOS for unique pressure:

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

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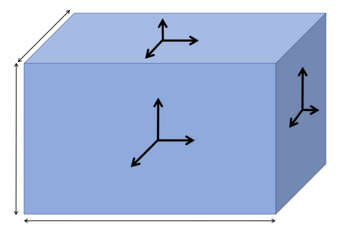
- may experience more complicated external forces that even include components parallel to the crystal surfaces.



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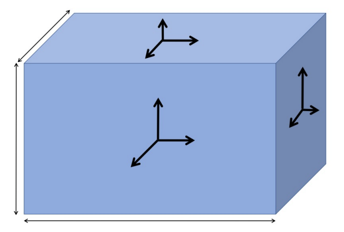

- Such complicated external forces can be described by the so-called Stress.

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- In order to keep a crystal in an equilibrium state, the external stress $\mathbf{S}$ must be symmetric: $S_{x,y} = S_{y,x}; \quad S_{x,z} = S_{z,x}; \quad S_{y,z} = S_{z,y}$.

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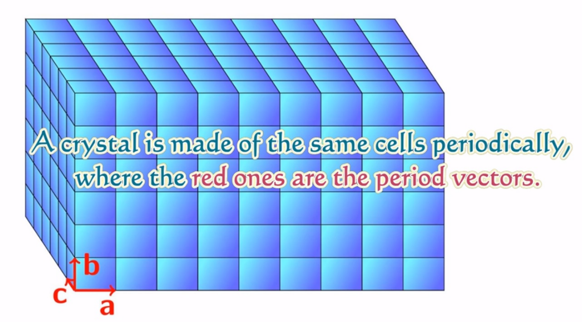
- For the special case of the same pressure P in all directions, the stress reduces to: $\mathbf{S} = -P\mathbf{I}$, with $\mathbf{I}$ being an identity tensor.

Period Vectors under External Stress



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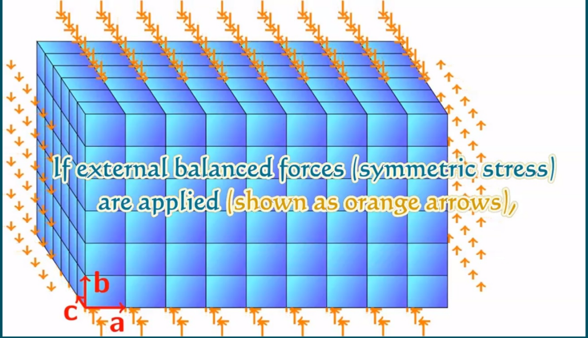

If external balanced forces (symmetric stress) are applied (shown as orange arrows),

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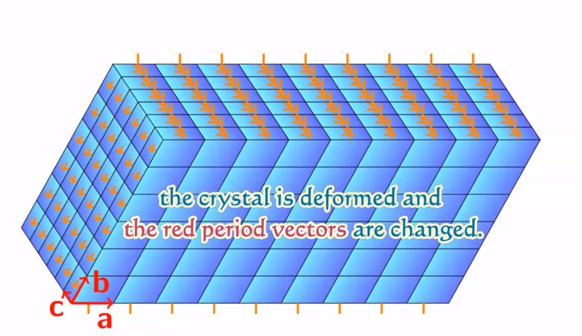

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- The recent publication in *The European Physical Journal Plus* (EPJP):

  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.

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

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- 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.

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  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:

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

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- 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 $(\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c})$.

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- 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

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

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

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

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- 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

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

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- 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

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- Even further relationships,

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

- Outline: 1

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- 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.

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- 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):

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

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- Combining this with our EOS

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  yields

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

Partition Function Z in the EOS

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

Partition Function Z in Classical Physics

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- 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

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

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- 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:

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

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  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,

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

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

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)

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

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

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  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

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

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

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

- Equation (2) becomes

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

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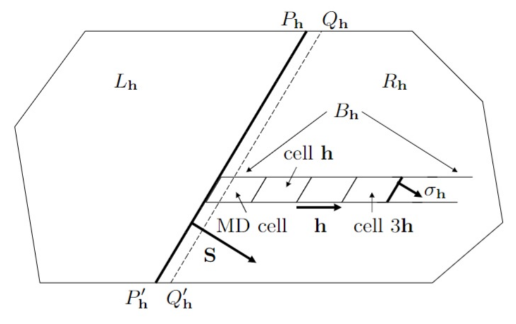
- is a very active research field that is closely related to the EOS. It usually applies Newtonian Dynamics throughout.
- It is common to apply the periodic boundary condition, i.e. to describe the system as if it were a periodic structure. The corresponding period vectors need to be dynamically simulated/determined. 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 $\mathbf{h}$:



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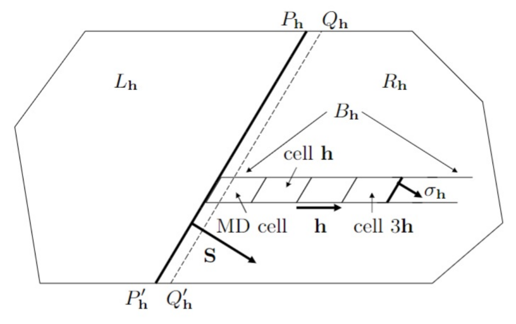

- Then applies the Newton’s Second Law on the right part.

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

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

  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.

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- 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:

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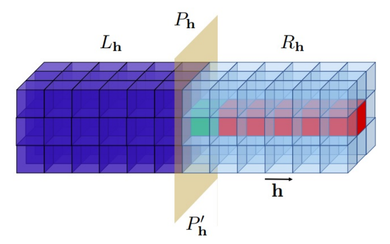
- So again the EOS of Equation (2) is the MMEC.

Molecular Dynamics Simulation

- In the above internal stress and Equation (51), the term: $-\left.\frac{\partial E_p}{\partial \mathbf{h}}\right|_{\mathbf{R}}$ 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:



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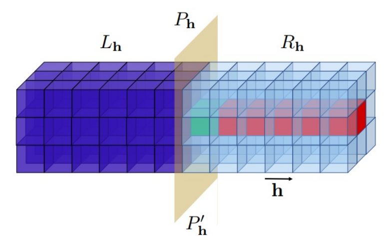

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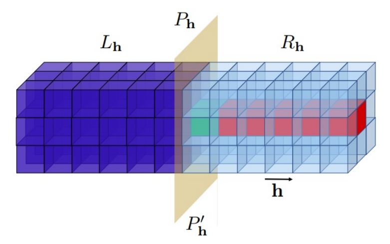

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- Many-body interactions: https://www.preprints.org/manuscript/201709.0030/v2

- Outline: 1

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  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

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

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- This follows from the relation presented earlier:

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

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- The total heat that needs to be supplied to the crystal in this process is
$$Q = E_{t,f} - E_{t,i} - W, \tag{14}$$
where the initial and final internal energies are $E_{t,i}$ and $E_{t,f}$, repsectively.

Piezoelectric/Piezomagnetic Processes

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- Since the new electric/magnetic field should be created by the new structure of the crystal, this EOS may help studying these phenomena.

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- 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

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

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- 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.

- 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

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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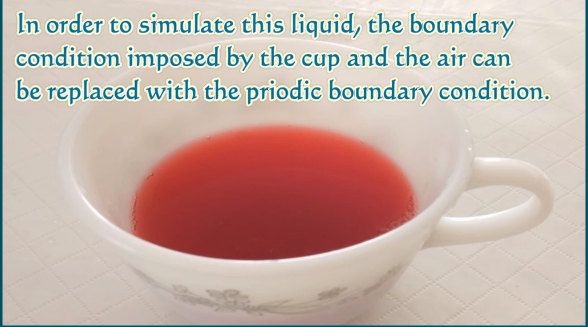

In order to simulate this liquid, the boundary condition imposed by the cup and the air can be replaced with the priodic boundary condition.

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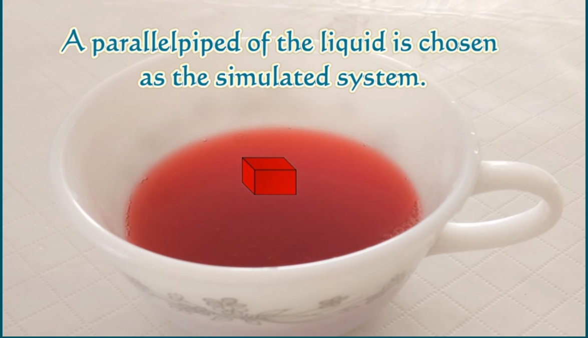

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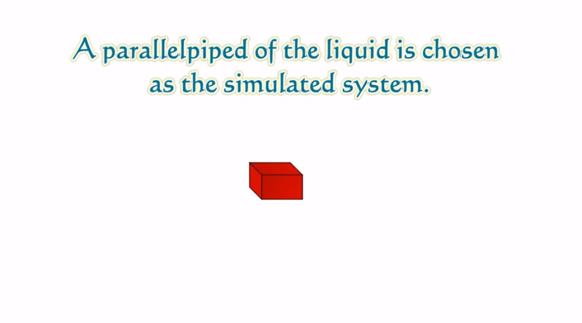

A parallelpiped of the liquid is chosen as the simulated system.

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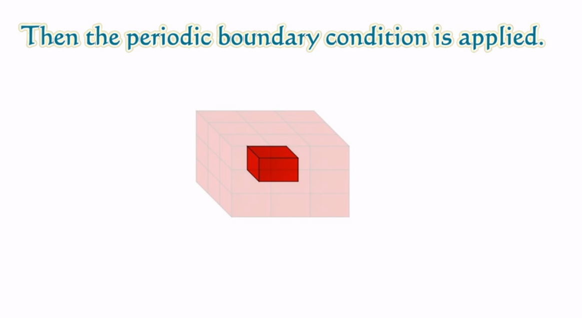

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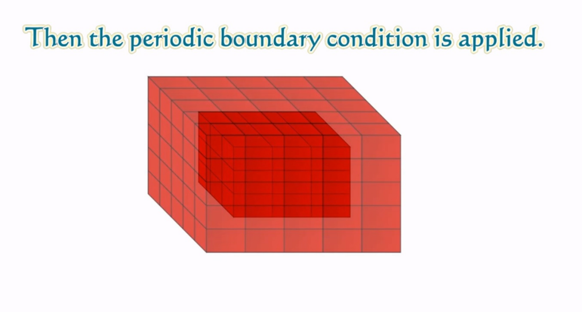

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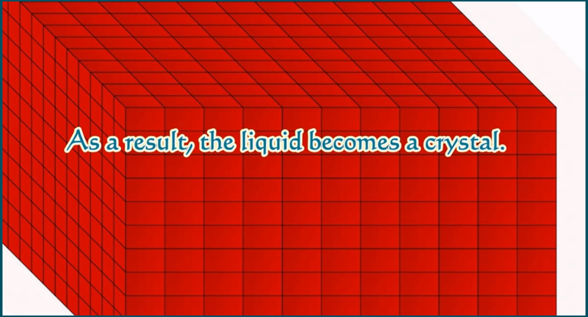
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- Under these circumstances, equation (2) and all conclusions based on it apply.

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- So the former is more detailed than the latter and implies the latter.

- Outline: 1

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- governs and supports the equilibrium states, is the MMEC, and is the EOS of material systems as well.

References and Supporting Materials

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Thank you very much for your attention!