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The Macroscopic Mechanical Equilibrium Condition Governing and Supporting Equilibrium States: the Physical Origin of the Equation of State
(Version 2)

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The Macroscopic Mechanical Equilibrium Condition can be shown to be the physical origin of the Equation of State of any material system, then can describe all thermodynamic quasi-equilibrium processes caused by the change of the external temperature and/or mechanical environment. If it cannot be satisfied, the system would be broken.

The Equation of State (EOS) of a gas, liquid, or solid has a pretty long history[1]. Then what is the physics behind it? The main purpose of the EOS is to yield the volume of a given material system under given external thermal and mechanical conditions. Since every such predicted volume is a determined unique real number, the EOS can only be for the system in a macroscopic equilibrium state. In such a situation, 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, the macroscopic mechanical equilibrium condition (MMEC) may shine more light into the system.

Now let us consider an ideal gas of $n > 0$ moles under given external pressure $P > 0$ and temperature $T > 0$. Further imagine that a pure geometric plane pp' cuts the gas into a left half and a right half system. The right half system (RHS) is determined 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 at any given time only microscopic particles inside this space and all such particles belong to the RHS. The left half system (LHS) is defined similarly. Let us further suppose that the ideal gas as a whole is in a macroscopic equilibrium state. However, from microscopic point of view, particles are running constantly as thermal motions. Each individual particle is not in an equilibrium state when it collides with another particle or the container.

When a microscopic particle crosses the plane pp' from the RHS into the LHS, roughly speaking, the RHS loses momentum in the left direction, equivalently acquires momentum in the right direction. If a microscopic particle crosses the plane pp' from the LHS into the RHS, the RHS acquires momentum in the right direction still once more. So the RHS constantly receives additional momentum in the right direction from the LHS, for both particle's moving in and out of the RHS. Let us call the time rate of the momentum change as the force associated with transport of momentum, as we did previously[2]. Supposing there is no collision happening for particles crossing the plane pp', the averaged pressure regarding the force associated with transport of momentum on the RHS due to particles running in and out of it can be derived as nRT/V, where R and V are the ideal gas constant and the gas volume respectively.

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 go back to their original side respectively. Here the force associated with transport of momentum is zero. However, actual forces in all the collisions are there now. The pressure of the total collision forces can also be derived as nRT/V. If some particles collide in the plane pp', and all others run through the plane pp', the pressure of the net of the force associated with transport of momentum and the collision forces should remain the same as nRT/V, 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. Let us call the above pressure as thermal pressure.

Since microscopic particles in any gas, liquid, and solid are always performing thermal motions, the thermal pressure applies to all real material systems. Let us further call the stress of the thermal pressure and other internal forces as the macroscopic internal stress. Then, the MMEC means that the macroscopic internal stress and the external stress balances each other.

Still for the ideal gas, further considering the container constantly injects momentum in the left direction into the RHS, the total momentum of the RHS is not noticeably changed from the macroscopic point of view. Then the RHS is also in a macroscopic equilibrium state and the MMEC applies. As a result, we get the well-known EOS: $P = nRT/V$. So the MMEC reproduces the EOS.

Let us now imagine that a real general material system in a macroscopic equilibrium state is cut into a great number of small, yet macroscopic pieces, with pure geometric planes. Then the macroscopic equilibrium state and the MMEC hold for each piece, implying that 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. Then a rigorous EOS can only 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.

As they both determine the geometry of the system, the MMEC/EOS can describe all thermodynamic quasi-equilibrium processes caused by the change of the external temperature and/or mechanical environment. If they cannot be satisfied, the system cannot be in an equilibrium state, then would be broken.

Consider a uniform metal rod in an equilibrium state. Later it is stretched by applying an additional balanced pair of pressures at its two ends along the length direction, in a quasi-equilibrium manner. How much the length will be increased for a given value of the extra pressures? It can be expected answered by the EOS in principle. Actually, the MMEC can, of course, decide it.

If a gas is heated under a constant external pressure, the inside increased temperature causes the internal pressure to be increased via the thermal pressure as well. In order to keep the internal pressure balancing the constant external pressure, the equilibrium distances between the microscopic particles of the system would be also increased. As a result, the volume of the system increases. If another gas is also heated, but contained inside a closed container with a fixed internal volume, the internal pressure would be increased. In order to keep the gas in an equilibrium state, the inner wall of the container should offer the balanced external pressure on the gas. If the system is heated unlimited, when the inner wall of the container fails to provide the external pressure on the gas balancing the internal pressure, the container would be broken. So these physical processes, which are expected to be explained by the EOS, can be described by the MMEC, with the thermal pressure being used.

The rigorous EOS for a system under the same external pressure from all directions is presented in almost all related books[3, 4]:

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

where $\beta = 1/(kT)$, and k and Z are the Boltzmann constant and the system partition function respectively. The right side of Eq.(1) is, in fact, the opposite value of the macroscopic internal pressure/stress of the system.

The equation determining the crystal period vectors (cell edge vectors $\mathbf{h} = \mathbf{a}$, or $\mathbf{b}$, or $\mathbf{c}$, forming a right-handed system), under arbitrary external stress $\mathbf{S}$, was derived in 2021 as[5]

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

where $\sigma_{\mathbf{h}}$ is the cell surface vector with respect to the period vector $\mathbf{h}$. Considering that the cell volume is determined by the period vectors as $V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$, Eq.(2) is the EOS of the crystal. It also applies to limit systems with the so called periodic boundary condition being applied.

In 2010, Tuckerman introduced the macroscopic internal stress $\mathbf{Y}$ for crystals in Equation (5.6.9) of his book *Statistical Mechanics: Theory and Molecular Simulation*[6], which can be rewritten as:

$$\mathbf{Y} = \frac{1}{\beta V}\sum_{\mathbf{h}=\mathbf{a},\mathbf{b},\mathbf{c}} \frac{\partial \ln Z}{\partial \mathbf{h}} \otimes \mathbf{h}. \tag{3}$$

Combining it with the EOS, Eq.(2), one can get

$$\mathbf{S} \cdot \sigma_{\mathbf{h}} = -\mathbf{Y} \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{4}$$

which explicitly means the MMEC:

$$\mathbf{S} + \mathbf{Y} = 0. \tag{5}$$

In fact, Eq.(2) was derived based on principles in statistical physics, then applies to both classical physics and quantum physics.

In pure classical physics, the dynamical equation of the crystal period vectors was derived based on Newton's Second Law in 2015 [2]:

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = (\pi + \mathbf{S}) \cdot \sigma_{\mathbf{h}} \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}), \tag{6}$$

with the macroscopic internal stress

$$\pi = \frac{1}{3V}\sum_{i=1}^{n} m_i \left|\dot{\mathbf{r}}_i\right|^2 \mathbf{I} - \frac{1}{V}\sum_{\mathbf{z}\in\mathrm{DOF}} \left(\frac{\partial E_{p,MD}}{\partial \mathbf{z}}\right) \otimes \mathbf{z}, \tag{7}$$

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, $\mathbf{I}$ is the identity tensor, DOF refers to all degrees of freedom of the system, and $E_{p,MD}$ is the total potential energy of a cell.

The corresponding EOS can be obtained straightforwardly by setting the accelerations of the period vectors in Eq.(6) as zero:

$$\pi + \mathbf{S} = 0, \tag{8}$$

which is also explicitly the MMEC.

For the special case of ideal gases in classical physics, both Tuckerman's macroscopic internal stress $\mathbf{Y}$ and the above macroscopic internal stress π become the thermal pressure: $\frac{1}{V}nRT\mathbf{I}$, reflecting the force associated with transport of momentum specifically.

In fact, the conclusion that the MMEC and the EOS should generate the same volume can also be drawn from the view of the degrees of freedom of the system.

[1] https://en.wikipedia.org/wiki/Boyle%27s_law
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[6] M.E. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, Oxford, 2010)