

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

Gang Liu

Independent Researcher, Kingston, Ontario, Canada, gl.cell@outlook.com, ORCID: 0000-0003-1575-9290

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 material may be broken.

The Equation of State (EOS) of a gas, liquid, or solid has a pretty long history[1]. The physics behind it should be explored. The main purpose of the EOS can be expected to yield the volume of the given material system under given external thermal and mechanical condition. Since the predicted volume is fixed, the EOS is for the system in a macroscopic equilibrium state, whether the volume in the equilibrium state is the same as that in any unequilibrium state or not. In such a situation, the macroscopic thermal and mechanical equilibrium conditions apply. The macroscopic thermal equilibrium condition is satisfied, as long as the macroscopic 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.

Let us now imagine that the system is cut into a great number of small, yet macroscopic pieces. Then the macroscopic equilibrium state and the MMEC hold, implying that the macroscopic internal stress at every macroscopic point of the system balances the external stress applied onto the system. Since it determines 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. Further considering that the MMEC is a well 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 may be broken.

If a gas is heated under a constant external pressure, the inside increased temperature causes the internal pressure to be increased 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 balanced external pressure on the gas, the container would be broken. So these physical processes can be explained by applying the MMEC, with the internal forces are influenced by the temperature.

The well-known EOS for an ideal gas may be written as  $P = nRT/V$ , where  $P$  is the external pressure,  $V$  is the vol-

ume of the gas,  $n$  is the amount of the gas (in moles),  $R$  is the universal gas constant, and  $T$  is the absolute temperature. Then the right side of the equation is actually the opposite value of the internal pressure.

The rigorous EOS for a real system under the same external pressure from all directions is presented in almost all related books[2, 3]:

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

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, also the opposite value of the internal pressure 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[4]

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

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*[5], which can be rewritten as:

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

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

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

which explicitly means the MMEC:

$$\mathbf{S} + \mathbf{Y} = 0. \quad (5)$$

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 [6]:

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

with the internal stress

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

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, 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 also be obtained straightforwardly by setting the accelerations of the period vectors in Eq.(6) as zero:

$$\pi + \mathbf{S} = 0, \quad (8)$$

which is also explicitly the MMEC.

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

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[1] [https://en.wikipedia.org/wiki/Boyle%27s\\_law](https://en.wikipedia.org/wiki/Boyle%27s_law)

[2] M.L. Bellac, F. Mortessagne, G.G. Batrouni, *Equilibrium and Non-equilibrium Statistical Thermodynamics* (Cambridge University Press, Cambridge, 2004)

[3] O.L. Anderson, *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford University Press, Oxford, 1995)

[4] G. Liu, *Eur. Phys. J. Plus* (2021),

<https://doi.org/10.1140/epjp/s13360-020-01010-6>

[5] M.E. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, Oxford, 2010)

[6] G. Liu, *Can. J. Phys.* (2015), doi:10.1139/cjp-2014-0518, arXiv:cond-mat/0209372 (version 16).