

The Maxwell rule in phase-transitions

*Dedicated to Prof. Henryk Zorski
on the occasion of his 70-th birthday*

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THE MAXWELL RULE, also known as the rule of equal areas, represents a basic notion in the phase transition processes. Although the rule might need amending for solids, it is treated as unquestionable for fluids. This belief relies on a thermodynamical argument. Namely, that the Gibbs thermodynamical potential should remain stationary during the transition process. Surprisingly, from the same thermodynamical argument, the Maxwell rule can be invalidated, even for fluids. Nonetheless, a revised form of the rule can be proposed.

1. Introduction

THE MAXWELL RULE applies to the pressure-volume or, in solids, to the stress-strain isothermal diagrams of materials undergoing a phase transition process. With specific reference to the Van der Waals equation [1-5], the liquid-vapour transition possibly occurs in the oscillating branch of the (P, V) state diagram. The rule states that: the state points of the (P, V) isothermal diagram have to be aligned along a horizontal isobaric segment during the transition. This segment divides the oscillating branch of the Van der Waals isothermal curve into two lobes of equal areas.

The rule can be easily extended to any phase transition.

A complementary method for phase transitions in solids and fluids deals with the isothermal families of the free energy diagrams [2]. The phase transition is believed to occur whenever the free energy loses the convexity property in one of its arguments. In this case, the linear convexity of the free energy is assumed to account for the phase transition process. Such a procedure is also known as the *method of the tangent* and is widely employed by metallurgists [2-6]. The method of the tangent and the Maxwell rule turn out to be equivalent one to the other as they represent two aspects of the same idea [6, 9]. Both rely on the stationarity of the Gibbs thermodynamical potential. However, the equivalence may fail whenever two different forms of the free energy, one for each phase respectively, exist. More specifically, the temperature dependence of the free energy may differ in the two phases whereas the volume dependence may not. From the mathematical standpoint, in this case the free energy is a continuous but not necessarily differentiable function of the temperature. From the physical

standpoint, one notices that the isothermal pressure-volume diagrams alone may show a deficiency in describing the process. Information about the specific heat in the two phases may also be of primary importance.

2. The Gibbs identity

The Maxwell rule is based on the Gibbs identity [2]. For homogeneous processes in simple fluids [10], the identity reads:

$$(2.1) \quad d\mathcal{E} = -P dV + T dS.$$

\mathcal{E} represents the internal energy, P the pressure, V the specific volume, T the temperature, S the entropy. The identity (2.1) suggests that \mathcal{E} should be understood as a differentiable function of V and S , P , by contrast, is usually given as a function of V and T in order to be consistent with the experimental diagrams. Thus, one is inclined to choose V and T rather than V and S as independent variables. Accordingly, the integrability conditions read:

$$(2.2) \quad \begin{aligned} \left. \frac{\partial \mathcal{E}}{\partial V} \right|_T &= T \left. \frac{\partial P}{\partial T} \right|_V - P, \\ \left. \frac{\partial P}{\partial T} \right|_V &= T \left. \frac{\partial S}{\partial V} \right|_T. \end{aligned}$$

One can introduce the free energy $\mathcal{F}(V, T) \equiv \mathcal{E} - TS$ by a Legendre transformation so that the following meaningful expressions

$$(2.3) \quad -P = \frac{\partial \mathcal{F}}{\partial V} \quad \text{and} \quad -S = \frac{\partial \mathcal{F}}{\partial T}$$

are attained.

By performing again a Legendre transform, one can introduce the Gibbs thermodynamical potential $G(P, T) = \mathcal{F} + PV$. Such a quantity is very useful for phase transition processes which occur at the thermomechanical equilibrium. In fact, as pressure and temperature do not vary during the process, G must also remain constant accordingly.

3. The Maxwell rule

During a process of phase transition there are regions in which two (or more) phases coexist [1-6]. In such regions the validity of an *a priori* settled constitutive law generally fails. By examining the experimental (P, V, T) diagrams of the related processes one may note that a bounded domain corresponds to such regions [1]. In such a domain any branch of the constitutive curves has to be

replaced by isobaric curves. Unfortunately, the boundary of this domain is *unknown*. The related thermomechanical problem is mostly concerned with finding this boundary. In the isothermal (P, V) diagrams the required boundary reduces to two points which have to be horizontally aligned along an isobaric segment. These two points are uniquely found by appealing to the stationarity condition for the Gibbs potential [1-6].

Having denoted by A and B the two boundary-points of interest in the isothermal (P, V) diagrams, one can write the following equation:

$$(3.1) \quad G_B - G_A \equiv \mathcal{F}_B - \mathcal{F}_A + \bar{P}(V_B - V_A) = 0.$$

Notice that $P_A = P_B \equiv \bar{P}$, according to the previous assumptions.

$\mathcal{F}_B - \mathcal{F}_A$ can be evaluated along the isothermal path $P(V, T_0)$, $V \in (V_A, V_B)$, $T_0 \equiv \text{constant}$. More specifically:

$$(3.2) \quad \mathcal{F}_B - \mathcal{F}_A = \int_{(V_A, T_0)}^{(V_B, T_0)} \left. \frac{\partial \mathcal{F}}{\partial V} \right|_{T_0} dV = - \int_{V_A}^{V_B} P(V, T_0) dV.$$

Note that

$$- \left. \frac{\partial \mathcal{F}}{\partial V} \right|_{T_0} \equiv P(V, T_0).$$

The unknowns \bar{P} , V_A and V_B are uniquely found by Eq. (3.1) with reference to the (P, V) diagrams.

A geometrical interpretation of Eq. (3.1) in the (P, V) isothermal diagram leads to the Maxwell rule of equal areas.

The weak point of these arguments resides in the choice of the path for the integral on the r.h.s. of the expression (3.2). In fact, the free energy is there evaluated along the isothermal branch of a curve which includes the so-called *spinodal region* (pressure increasing with increasing volume). Such a branch does not represent *physically reversible processes*. A possible different choice may be that of performing the path integral along any other path out of the transition region. Such a path needs not be an isothermal curve; it is only required to represent a reversible process whose initial and final states are at the same temperature and pressure.

Assume now that the proposed path of integration crosses the border between the pure phase domains in the (T, V) diagram. The free energy may change its form in the temperature dependence passing across such a border. As the border is *a priori known*, one is able to evaluate the path-integral of interest.

In the specific case of the V.d.W. curves one achieves the following final result:

$$(3.3) \quad \mathcal{F}_B^* - \mathcal{F}_A = - \int_{(V_A, T_0)}^{(V_B, T_0)} P(V, T(V)) dV + \lambda(T_0).$$

The superscribed star in \mathcal{F}_B^* stresses the different form of \mathcal{F}_B^* with respect to \mathcal{F}_A .

The reader interested in further details is referred to the paper by KAHL [7].

The expressions (3.2) and (3.3) differ from each other by the amount $\lambda(T_0)$. Should the two forms of the free energy coincide, $\lambda(T_0)$ would vanish. In this circumstance the equivalence between the aforementioned expressions is completely recovered. The quantity $\lambda(T_0)$ is related to the different forms of the specific heat in the two pure phases.

One can summarize the result by remarking the following. The free energy \mathcal{F} is continuous across the border between the pure phases, but possibly not differentiable with respect to temperature; at least, not twice differentiable.

The expounded argument can be extended to any two-phase diagram, provided that no hysteresis occurs and no progress of transition fronts [4, 6, 8, 9] takes place. The Gibbs thermodynamical potential still remains stationary, though the Maxwell geometrical rule of equal areas may not hold any longer. Nevertheless, an amendment to the Maxwell rule can be proposed in the presence of *spinodal regions*. The amended rule could be restated as follows: the areas of the cut lobes are possibly unequal but may differ from one another by a quantity which depends only on the temperature.

4. Final comments

The Maxwell rule can be questioned even for the classical Van der Waals diagrams for fluids. The failure of such a basic rule can be attributed to the two different forms the free energy may exhibit in the two phases.

In solids and in crystals the phase transition processes can be much more involved. For thermoelastic materials, the free energy depends on the strain (a second order tensor) whereas in fluids the only geometrical quantity considered is the specific volume (a scalar quantity). The strain addresses the geometrical compatibility conditions and, in turn, the notion of *coherence* [2-4, 6, 8, 9]. Additional remarkable differences can be envisaged with respect to fluids. In fact, the notions of *natural state*, of *self-strain* and of *strain energy* may be relevant in solids. By contrast, they are meaningless in fluids. Such notions lead to different forms of the free energy, each for one of the pure phases, even in the simplest one-dimensional problems of phase transition [6, 9].

Hence, the validity of the Maxwell rule is once more undermined.

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