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Phenomenological and Theoretical Analysis of Phase Equilibrium in Relativity

Marko Popovic

Abstract – *One component thermodynamic system with two phases in equilibrium was analyzed. Phenomenological it was shown that it must remain in equilibrium during movement. Theoretically starting from the Clapeyron equation it was shown that the slopes (dp/dT) of the phase boundaries are Lorenz invariant. The molar effective volumes of the phases must be Lorenz invariant, for the phases to remain in equilibrium. The Clapeyron equation is valid in relativistic thermodynamics, if effective volume is taken into consideration.*

***Keywords**: Phase Equilibrium, Relativity, Clapeyron Equation, Temperature, Entropy, Lorentz Fitzgerald Contraction*

I. Introduction

Special theory of relativity was published in 1905. One of its consequences is relativistic length contraction [1] given as:

$$x' = x\sqrt{1-\frac{v^2}{c^2}}$$

This phenomenon real [2]-[4] or apparent [5]-[8] causes relativistic volume contraction given as:

$$V' = V\sqrt{1-\frac{v^2}{c^2}}$$

Second consequence of special relativity is transformation for temperature. This transformation was the subject of scientific disagreement for more than 100 years. So the crucial question of the relativistic transformation for temperature is a great problem for thermodynamics. The question of relativistic effects on thermodynamic systems was first analyzed by Planck [9] in 1907. So by Planck and early Einstein:

$$T' = T\sqrt{1-\frac{v^2}{c^2}}$$

In 1952 Einstein turned from the Planck-Einstein transformation formulas (1907), and suggested new transformations:

$$T' = \frac{T}{\sqrt{1-\frac{v^2}{c^2}}}$$

H. Ott [10] proposed the same equation some years later (1963), independently of Einstein´s results.

Landsberg stated that “temperature should be Lorentz invariant”. But, later, he restarted the problem by saying that it is impossible to obtain a general transformation of temperature [11]. Lorentz invariance of temperature was concluded by other authors as well: “The non-existence of a relativistic temperature transformation is due to the fact that an observer moving in a heat reservoir cannot detect a blackbody spectrum.” [12]. Also “All thermodynamic relations become Lorentz-invariant” have been made [13]. “One has to conclude that the temperature is invariant with Lorentz transformations” [14].

So mathematically:

$$T' = T$$

Further, Lindhard has shown from basic thermodynamics that temperature and entropy are invariant in special relativity.[13] “There is no universal relativistic temperature transformation” claims Bormashenko [15]. In the Avramov’s paper we can find another conclusion:”If temperature is invariant with speed, then entropy with respect to the Boltzmann constant is not. This put’s serious problems on the statistical physics” [16].

Popovic claims: “The easiest way to explain Lorentz invariance of temperature is to conclude that the process is isotherm.”[17]

Tolman stated that pressure is Lorentz invariant: “We at once obtain the simple result $p=p_0$ as the transformation equation for pressure”[18] So $p = p'$

The pressure invariance is a generally accepted fact. And in the last twenty years most authors conclude that temperature is Lorentz invariant as well.

II. Phenomenological Consideration

Let's consider a closed container filled with one substance distributed in two phases, which are at equilibrium. It represents a closed thermodynamic system with two phases in equilibrium, containing one component. There are two observers located in two reference frames. The observer 1 and the thermodynamic system are in inertial system K'. The inertial system K' is in relativistic movement. Observer 2 is in inertial system K, which is relatively resting. The observer 1 notices two phases in the container are in equilibrium, and sees an interface between them. The observer 2 notices the same state which means, the same interface. This is in accordance with the fact that a physical process occurs independently of the presence of observers.

III. Theoretical Consideration

The fact that two phases are in thermodynamic equilibrium in the system means that the current state of the system lies on a phase boundary line in the p-T diagram. The slope of the phase boundary line is given by Clapeyron equation:

$$\frac{dp}{dT}=\frac{S_{\alpha,m}-S_{\beta,m}}{V_{\alpha,m}-V_{\beta,m}} \tag{1}$$

where p is pressure, T is temperature, $S_{\alpha,m}$ and $S_{\beta,m}$ are the molar entropies of the phases α and β respectively, and $V_{\alpha,m}$ and $V_{\beta,m}$ are the molar volumes of the phases α and β respectively. This equation is valid for observer 1 cituated in K' frame of reference. For observer 2 cituated in K, who notices relativistic effects, it takes form:

$$\left(\frac{dp}{dT}\right)'=\frac{S'_{\alpha,m}-S'_{\beta,m}}{V'_{\alpha,m}-V'_{\beta,m}} \tag{2}$$

where $(dp/dT)'$ is relativistic slope of the phase boundary line. $S'_{\alpha,m}$ and $S'_{\beta,m}$ are the molar entropies of the phases α and β respectively noticed by observer 2 in K, and $V'_{\alpha,m}$ and $V'_{\beta,m}$ are the molar volumes of the phases α and β respectively noticed by observer 2 in K. Entropy is Lorentz invariant according to Planks theorem of Entropy invariance [9] and supported by others authors [15]-[19], which applies to molar entropies of the phases too:

$$S'_{\alpha,m}=S_{\propto,m} \tag{3}$$

$$S'_{\beta,m}=S_{\beta,m} \tag{4}$$

We combine (3) and (4) with (2), so:

$$\left(\frac{dp}{dT}\right)'=\frac{S_{\alpha,m}-S_{\beta,m}}{V'_{\alpha,m}-V'_{\beta,m}} \tag{5}$$

Volume transforms according to special relativity [20], which for molar volumes takes the form:

$$V'_{\alpha,m}=V_{\alpha,m}\sqrt{1-\frac{v^2}{c^2}} \tag{6}$$

$$V'_{\beta,m}=V_{\beta,m}\sqrt{1-\frac{v^2}{c^2}} \tag{7}$$

By combining (5) with (6) and (7) we obtain:

$$\left(\frac{dp}{dT}\right)'=\frac{S_{\alpha,m}-S_{\beta,m}}{\left(V_{\alpha,m}-V_{\beta,m}\right)\sqrt{1-\frac{v^2}{c^2}}} \tag{8}$$

Putting together (1) and (7) gives us an equation which relates the slope of the phase boundary line noticed by observer 1 and the phase boundary line noticed by observer 2:

$$\left(\frac{dp}{dT}\right)'=\left(\frac{dp}{dT}\right)\frac{1}{\sqrt{1-\frac{v^2}{c^2}}} \tag{9}$$

Let's now consider the physical meaning of equation (9). It means that the phase boundaries undergo relativistic transformations. This means that two observers should notice different phase diagrams for the system. The state of the system is given by a point A in the p-T diagram (Fig. 1). The position of this point is the same for both observers, because of the Lorenz invariance of pressure [9],[10],[15],[18] and temperature [12]-[17]. The thing that is different for them is the position of phase boundary, according to (9). The observer 1 notices no change in the phase boundary, and for him the state of the system rests on it. So he notices two phases in equilibrium in the system. We can see this on the diagram, where the state of the system is given by point A, and it rests on the full line, which is the phase boundary noticed by observer 1 in K'. But for observer 2 the phase boundary has changed, so for him the state of the system doesn't rest on it. This means that he notices only one phase in the system. The point A which is the same for both observers doesn't lie on the dashed line which is the phase boundary noticed by observer 2 in K.

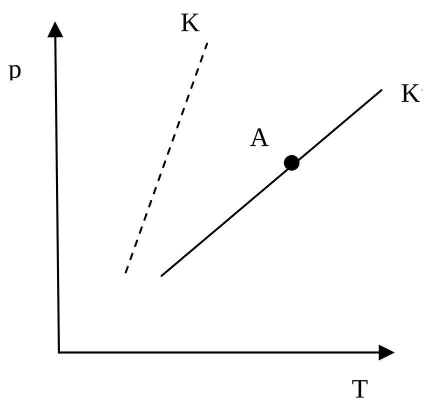

Fig. 1. Theoretical illustration for a phase diagram for a system at relativistic movement

From the consideration above we see that the consequence of equation (9) is that two observers notice one system in two different states. Observer 1 sees it containing two phases, while the observer 2 notices only one phase. This is not logic and therefore not possible. So there must be another solution.

IV. Solution

Let's start from the conclusion we derived by consideration above: There is no relativistic phase boundary transformation. So the equation (9) must be replaced by:

$$\left(\frac{dp}{dT}\right)=\left(\frac{dp}{dT}\right)' \quad (10)$$

Notice that pressure is Lorentz invariant according to Plank [9], Tolman [18] and other autors [11]-[23] so *p=p'*, and temperature is also Lorentz invariant according to [11]-[17],[19],[21],[22], so *T=T'*. Further, "The simpliest relativistic generalization of thermodynamics which we describe leads naturally to choice of Lorentz invariant temperature" [23]. The same paper confierms the Planks theorem of Entropy invariance"The number of microstates of a system is not dependent on its state of motion relative to an observer, so that implied dependence of Entropy on momentum is misleading formalism"[23]

Then if we insert equations (1) and (2) into (10) it leads:

$$\frac{S_{\alpha,m}-S_{\beta,m}}{V_{\alpha,m}-V_{\beta,m}}=\frac{S'_{\alpha,m}-S'_{\beta,m}}{V'_{\alpha,m}-V'_{\beta,m}} \quad (11)$$

If we take into account (3) and (4) we obtain:

$$V_{\alpha,m}-V_{\beta,m}=V'_{\alpha,m}-V'_{\beta,m} \quad (12)$$

This equation is the main condition for the slopes of the phase boundaries to be Lorenz invariant. The problem is that this equation seems to be in conflict with (6) and (7). Yet it must be true because it's the condition for phase equilibrium to be noticed by both observers. We see that it is impossible for the entropy and phase equilibrium to be Lorentz invariant, while volume is Lorenz covariant. The solution is to replace volumes in equation (1) and (2) with effective volumes as suggested in [21]. In that case we obtain:

$$\left(\frac{dp}{dT}\right)=\frac{S_{\alpha,m}-S_{\beta,m}}{V_{eff,\alpha,m}-V_{eff,\beta,m}} \quad (13)$$

$$\left(\frac{dp}{dT}\right)'=\frac{S'_{\alpha,m}-S'_{\beta,m}}{V'_{eff,\alpha,m}-V'_{eff,\beta,m}} \quad (14)$$

where $V_{eff,\alpha,m}$ and $V_{eff,\beta,m}$ are the molar effective volumes of phases α and β respectively noticed by observer 1, while $V'_{eff,\alpha,m}$ and $V'_{eff,\beta,m}$ are the effective volumes of phases α and β respectively noticed by observer 2. The effective volume [21] is in better accordance with the modern understanding of relativistic length contraction [22]. So, while the system moves at relativistic speeds, its length transforms, together with its metric volume, but its effective volume doesn't transform. The effective volume is a macroscopic parameter of the system created to take in to account that systems state functions such as pressure, temperature, and entropy are Lorenz invariant. While it's metric volume is Lorenz covariant. An important property of the effective volume is that it is Lorentz invariant. This applies to molar effective volumes of the phases:

$$V'_{eff,\alpha,m}=V_{eff,\alpha,m} \quad (15)$$

$$V'_{eff,\beta,m}=V_{eff,\beta,m} \quad (16)$$

So we see that equation (13) is completely in accordance with the concept of effective volume (15) and (16). Since the effective volume is Lorenz invariant, we conclude that the slopes of the phase boundaries are also Lorenz invariant. This way we conclude that both observers see two phases in equilibrium.

So the problem in the phenomenological consideration has been solved.

V. Conclusion

The slopes (*dp/dT*) of the phase boundaries are Lorenz invariant. The molar effective volumes of the phases must be Lorenz invariant, for the phases to remain in equilibrium. The Clapeyron equation is valid in relativistic thermodynamics, if effective volume is taken into consideration.

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Authors' information

Faculty of Chemistry,
University of Belgrade,
Belgrade, Studentski trg 12-16,
Serbia.
E-mail: popovic.pasa@gmail.com

Marko Popovic Born in Belgrade, Serbia in 1990. He is a student of Faculty of chemistry, Belgrade University. His area of interest is Chemical Thermodynamics, Biothermodynamics and relativistic Thermodynamics.
He has published in Thermal Science, International Review on Chemical Engineering, and International Review of Natural Science. Marko Popovic is member of American Chemical Society (ACS), International Association of Chemical Thermodynamics (IACT), and Serbian Chemical Society (SCS)