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THERMODYNAMICS OF NEGATIVE ABSOLUTE PRESSURES

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ABSTRACT

Here we show that the possibility of negative absolute pressure can be built into the axiomatic thermodynamics, analogously to the negative absolute temperature. There are examples for such systems (GUT, QCD) possessing negative absolute pressure in such domains where it can be expected from thermodynamical considerations.

АННОТАЦИЯ

В работе показано, что существование отрицательного абсолютного давления находится в соответствии с аксиоматикой термодинамики, подобно существованию отрицательной абсолютной температуры. Приводятся примеры таких систем (теория большого объединения, квантовая хромодинамика), в которых появление отрицательного давления происходит в областях, где оно ожидается и на основании термодинамических соображений.

KIVONAT

Megmutatjuk, hogy a negativ abszolut nyomás összefér az axiomatikus termodinamikával, hasonlóan a negativ abszolut hőmérsékletekhez. Ilyen rendszerekre vannak példák (GUT, QCD), és azokban a negativ nyomás olyan tartományokban lép fel, ahol a termodinamikai megfontolásokból várható is.

1. INTRODUCTION

While the pressure of all familiar kinds and states of matter is non-negative, various models do predict negative pressures in some exotic states. The simplest classical example is the overheated van der Waals fluid [1], but there are examples in nuclear physics too, both below normal nuclear density [2] and above [3] and the field theoretically based Walecka equation of state [4] suggests that at least the first case is not an artefact of unphysical assumptions. Similarly, states of negative pressure are suggested by the perturbative QCD at low temperatures and densities [5]-[7] and in GUT's, where these states are explicitely used for eliminating the monopole problem by exponential inflation of the Universe (see e.g. Ref. [8]). However, the physical meaning of such states is often doubted, they are suspected to be results of theories used beyond their validity.

In thermodynamics, states of negative pressure are regarded as not stable but metastable, belonging to a local but not global maximum of the entropy [1]; since $(\partial S/\partial V) < 0$, a spontaneous collapse can be expected. Nevertheless, even then, the $p < 0$ can exist for a limited time, so this argumentation is not decisive in dynamical calculations. In dynamical situations, Danielewicz states [2] that the existence of $p < 0$ states seems awkward, but it is not excluded by any law of nature, although the hydrodynamic flow is unstable there for droplet formation [2], [8]-[10]. In some cases, in fact, the $p < 0$ states occur at the limit of an approximation (the perturbative treatment of QCD ceases to be valid at temperatures and densities; in GUT $p < 0$ states are often calculated , the high energy expansion of the effective potential, which is far from being obvious after the symmetry-breaking phase transition), and they are almost generally connected with phase transitions in such a way that a slow equilibrium phase transition would eliminate them (an exception is in Ref. [3], however, see the argumentation in Ref. [9]). Thus it seems that this question needs a model-independent approach.

Of course, the question of the existence of $p < 0$ states (which may be thermodynamically metastable and hydrodynamically unstable) must be very carefully distinguished from the thermodynamically unstable situation when the compressibility is negative. Therefore, in this paper we restrict ourselves only to situations where the matrix of the second derivatives of the entropy is negative definite.

2. THE DEFINITION AND THE ENERGY-MOMENTUM TENSOR OF THE VACUUM

Since in QCD the negative pressure is connected with the difference between a "physical" and a "Fock" vacuum, and similarly in GUT with a distinction between a "true" and a "false" vacuum, let us start with the definition of the "physical" or "true" vacuum.

The basic assumption of General Relativity is a close relation between the curvature of spacetime and the distribution of the matter. So there has to exist a tensorial equation

$$R_\Gamma(g_{ik}) = Q_\Gamma(\text{matter distribution}) \qquad (2.1)$$

where Γ stands for some tensorial indices, g_{ik} is the metric tensor, and Q_Γ is some tensor for the matter. The operation simbolized by R_Γ must contain at least second derivatives in order to get the Newtonian limit [11]. Since Q_Γ is equal with an expression of g_{ik} alone, it will fulfil some balance equations, in the simplest case when R_Γ is a second order tensor of not higher than second derivatives, then we arrive at the equation [12]

$$R_{ik} - \frac{1}{2}g_{ik}R + \lambda g_{ik} = \kappa T_{ik} \quad , \qquad (2.2)$$

where R_{ik} is the Ricci-tensor [11], R is its trace, $\kappa = -8\pi\gamma/c^4$, while λ is an undefined constant, the so-called "cosmologic constant".

Then, by construction, T_{ik} fulfils the balance equations

$$T^{ir}{}_{;r} = 0 \quad , \qquad (2.3)$$

where the semicolon stands for covariant derivation, so in flat spacetime one can get four conserved quantities by integrating T_{ik}. Since four such quantities are already known, namely the energy and the momenta, formed from the energy-momentum tensor, T_{ik} is to be identified with the energy-momentum tensor.

In the simplest case (for fluids) T_{ik} has the form [11]

$$T_{ik} = (\rho + p)u_i u_k + pg_{ik} \quad , \qquad (2.4)$$

where ρ and p stand for some energy density and pressure, respectively, and u_i is the flow velocity.

Now, one can see that there is no unique connection between the curvature and such quantities as ρ and p, because the constant λ is undefined [7]. Nevertheless, it seems that there exists a preferred gauge. Namely, observations seem to show that there exist regions where the spacetime is approximately flat, as in the interstellar space far from the masses. Then, from Eq. (2.2) there

$$T_{ik} = -\frac{\lambda}{\kappa}g_{ik} \quad . \tag{2.5}$$

Then General Relativity permits to use such a convention where ρ and p vanishes in this special case, and $\lambda = 0$. This special state of matter is called "physical vacuum" in this paper.

The possibility of such a preferred gauge is not a priori guaranteed. For example, in some Universe models (as the de Sitter solution) $\lambda \neq 0$, which is, from the viewpoint of General Relativity, equivalent with the assumption that $\lambda = 0$, but $\rho = -p \neq 0$ for the interstellar space. Nevertheless, there are no evidences for such cases, so we can stop here.

Having the zero point of the energy fixed in such a way, the value of the energy-momentum tensor is unique for any kind of matter. Now, there exist some general principles imposing some constraints on T_{ik}. E.g. causality is a limit for the derivative $dp/d\rho$ [10], but such conditions do not restrict zero points of scales. The algebraic constraints are called energy positivity conditions, requiring that the energy density seen by any observer be nonnegative. The strongest proposed energy condition of immediate physical meaning is the dominant energy condition:

$$\begin{aligned} T_{rs}v^r v^s &\geq 0 \\ T_{ru}v^u T^{rs} v_s &\geq 0 \end{aligned} \tag{2.6}$$

for any timelike unit v^i [13], i.e. that the energy density is nonnegative and dominates the energy flux for any observer. For an energy-momentum tensor of form (2.4) Conds. (2.6) lead to

$$\begin{aligned} \rho &\geq 0 \quad , \\ \rho + p &\geq 0 \quad . \end{aligned} \tag{2.7}$$

So, the energy positivity condition of General Relativity does impose a lower bound on p, but it is negative.

It is necessary to note that energy conditions are principles summarizing our common sense about energy-momentum tensors; they cannot be proven from some more fundamental facts, althouth there are some particular cases when they prevent paradoxical behaviour of the matter or of the space-time [13].

3. THERMODYNAMICS OF STATES OF NEGATIVE ABSOLUTE PRESSURE

In thermodynamics the zero point of the pressure scale is generally taken from non-thermodynamic sources [14]. For example, in one of the most detailed axiomatic treatment of thermodynamics [15] Tisza says: "The intensity conjugate to the volume is the negative pressure -p. This follows from the requirement that in the absence of caloric and chemical changes the equation

$$dU = TdS - pdV + \sum_j \mu_j dN_j$$

should reduce to the well-known energy relation of fluid mechanics."

Nevertheless, there are cases when the zero points of the scales of the intensive parameters (e.g. of -p) can be defined on a postulatory basis. A postulate system summarizing the fundamental properties of normal thermodynamic systems has been proposed by Callen [16]:

Postulate I: There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U, the volume V, and the mole numbers $N_1, N_2, \ldots, N_r$ of chemical components (extensive parameters).

Postulate II: There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property. The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

Postulate III: The entropy of a composity system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.

Postulate IV: The entropy of any system vanishes in the state for which

$$\frac{\partial U}{\partial S} = 0 \quad ,$$

that is, at the zero of temperature.

The above postulate system defines the entropic intensive parameters Y_i,

$$Y_i = \frac{\partial s}{\partial \rho^i} \quad , \tag{3.1}$$

where s is the entropy density and ρ^i stands for the i^{th} extensive density, in the following form:

$$Y_i = \int_{\rho^{ko}}^{\rho_k} g_{ik} d\rho^k + Y_{io}(\rho^{ko}) \tag{3.2}$$

and

$$g_{ik} = -\frac{\partial^2 S}{\partial\rho^i \partial\rho^k} \qquad (3.3)$$

is defined for the system under investigation up to a multiplicative constant by the Postulate system, nevertheless Y_{io} is not defined [17]. (From hence we use the Einstein index convention, i.e. there is a summation to any kind of indices occurring twice, both above and below [11].)

By shifting the zero points of the entropic intensive parameters, S changes as

$$S' = S + (Y_{io}' - Y_{io})X^i \quad , \qquad (3.4)$$

where X^i stands for the extensive parameters, so the entropy is not unique, which fact was first discussed by Guggenheim [18], in case of $Y_1 = 1/T$. For this case the problem can be solved by an additional [17].

Postulate V:

$$\lim_{E/V\to\infty} \frac{\partial S}{\partial E} = 0 \quad .$$

Nevertheless, there are real systems for which Postulate III does not hold, the entropy has a maximum at finite E/V [19], [20]. Such systems are called special systems [21], in contrast to the normal systems obeying Callen's postulate system, when E/V can be (asymptotically) infinite in the system.

Now, consider a special system in which E/V possesses an absolute upper bound. Then Postulate V cannot be imposed on the system, and Eq. (3.4) shows that the maximum of S can be shifted to any convenient value of E. Then, by putting sufficient energy into the system, one can pass beyond the maximum, reaching negative 1/T values.

Summarizing the above statements: for systems with the possibility of infinite energy density Callen's postulate system can be supplemented by a fifth postulate, then the postulate system is necessary and sufficient for unique thermodynamic description, and the zero point of $Y_1 = 1/T$ can be reached only asymptotically. For systems with an absolute upper limit in E/V Postulate III has to be weakened, Postulate V cannot be imposed, and the remaining Postulates permit any zero point of the 1/T scale. Then, establishing a thermal contact with a normal system, the zero point is fixed for the special system too, but this is not an asymptotic point, so the temperature can be negative. Such systems actually do exist (e.g. the nuclear spins in LiF, [19], [20]). For further discussion see Ref. [22].

The same method can be applied to define the zero point of $Y_2 = -p/T$. The necessary additions to the postulate system for getting a unique pressure scale compatible to the mechanics are:

Postulate III: ... and the entropy is a monotonously increasing function of V too.

Postulate VI:

$$\lim_{V/E\to\infty} \frac{\partial S}{\partial V} = 0 \quad .$$

Such a system, if surrounded by the physical vacuum, spontaneously expands, asymptotically goes to infinite volume, and the zero point of the pressure scale belongs to this asymptotic state. This definition of $Y_2 = 0$ is obviously consistent with the mechanical definition of p, and similarly, with the chosen preferred gauge of General Relativity discussed in the previous Section.

Now, consider a system in which the energy density has a positive absolute minimum. Then the new form of Postulate III is too strong and Postulate VI cannot be applied, but without them the postulate system does not determine the zero point of p, similarly to the previously discussed case of T. Mechanical contact with a normal system yields the zero point of the pressure scale even for such a system, nevertheless the postulates do not guarantee the positivity of the pressure in the whole physical domain of the extensive parameters, and so negative pressures can be expected for such systems.

4. EXAMPLES FOR SPECIAL SYSTEMS

In this Section we are going to discuss three cases when at least some simplified models of physical systems possess lower bounds for the energy density, namely Quantum Chromodynamics, Grand Unified Theory and nuclear matter.

In the perturbative limit of QCD the pressure of the gas has the form [6], [23]

$$p = \frac{37}{90}\pi^2 T^4 + \mu^2 T^2 + \frac{1}{2\pi^2}\mu^4 - B \quad . \tag{4.1}$$

This perturbative limit is reached at high quark densities or temperatures, and there the system imitates free particles on a Fock vacuum, which, of course, does not possess any immediate relation to the physical vacuum, and the energy difference of the two vacua is B. According to elementary facts as the existence of nucleons, B > 0. At low densities or temperatures interaction terms occur, see e.g. Ref. [24], but here we restrict ourselves to this simplified model.

Calculating the energy density from Eq. (4.1) one gets:

$$\varepsilon = \frac{1}{3}(p + B) + B \quad , \tag{4.2}$$

(In order to express s as a function of ε and n one should solve a cubic equation, and the results would not be too transparent.) Now, Eq. (4.1) shows that $p + B \geq 0$, so $\varepsilon \geq B$. By other words, the energy density of a perturbative QCD medium is bound from below by the energy density of the Fock vacuum, B. Then the limit in Postulate VI is meaningless, so thermodynamic postulates do not determine the zero point of the pressure.

Of course, we are not in the position to establish a real mechanical contact between the perturbative QCD plasma and a normal system. Nevertheless, one can calculate the conditions for phase equilibrium between nuclear and quark matter (assuming that at that density the perturbative picture still valid, which is not obvious). If we had some information about the nuclear density at the phase transition, this calculation would match the pressure scales. The fact that at normal nuclear density this transition cannot be seen, imposes a lower, positive bound on B [5], [7], [25].

With positive B, Eq. (4.1) leads to negative pressures at low μ and T. Of course, it would be difficult to decide if the perturbative treatment is valid there. Nevertheless, one can conclude that for perturbative QCD plasma Postulate VI cannot be applied, and if the fact that the energy density has a positive lower bound is physically correct, then elementary thermodynamic considerations indicate pecularities in the pressure scale.

The second example is GUT. In such theories the self-interaction of the Higgs sector is described by a quartic polynomial potential, having two minima and one maximum, thus generating spontaneous symmetry breaking. At high temperatures the Higgs expectation values vanish, but there is a phase transition temperature below which the expectation values get near to the location of one of the minima [26]. Consider, for simplicity's sake, one single Higgs boson. Then

$$V(\phi) = -\frac{1}{2}\mu^2\phi^2 - \frac{1}{3}\varepsilon\mu\phi^3 + \frac{1}{4}\lambda^2\phi^4 + V_o \quad , \tag{4.3}$$

where μ is the mass scale of the theory (in the order of 10^{15} GeV), ε and λ are dimensionless numbers. If $T \ll \mu$, the free energy of the system is minimal if

$$\phi \simeq \phi_\pm = \frac{\mu}{2\lambda^2}(\varepsilon \pm \sqrt{\varepsilon^2 + 4\lambda^2}) \quad , \tag{4.4}$$

where

$$V = V_\pm = -\frac{\mu^4}{96\lambda^6}(\varepsilon \pm \sqrt{\varepsilon^2 + 4\lambda^2})^2(6\lambda^2 + \varepsilon^2 \pm \varepsilon\sqrt{\varepsilon^2 + 4\lambda^2}) + V_o \quad . \tag{4.5}$$

If we accept that now the matter of the Universe occupies the deeper minimum, then V_o is to be chosen in such a way that $V_+ = 0$, when $V_- > 0$.

Now, let us assume that in the past there was a period when the Universe occupied the other minimum. Then there the energy density was bound from below by $\Delta = V_- > 0$. So again Postulate VI cannot be applied on the system. In fact, calculating the pressure, it is negative [26], [27]. The mechanical contact is established by phase transition again, because the true vacuum is reachable via thermal fluctuations or tunnelling. The negative pressure of these states results an accelerating expansion of the Universe, and in the original "inflationary scenario" [27] this accelerating expansion is regarded as the mechanism diluting the primordial massive monopoles below the present observational limit.

Ref. [28] gives an approximation for the free energy of the system, which is of limited validity, but quite sufficient for demonstrating the properties of the "false vacuum". Removing a term which would lead to negative entropy at low temperatures,

$$p = \alpha T^4 - \Delta \quad ; \qquad \alpha = \frac{\pi^2}{90} \quad , \tag{4.6}$$

whence

$$S = 3^{-3/4} 4\alpha^{1/4} (E - V\Delta)^{3/4} V^{1/4} \quad , \tag{4.7}$$

where V is the volume. Now, one can see that S has a maximum as a function of V at $E = 4V\Delta$, so the additive part of Postulate III cannot be applied on the system too. Again, the negative pressure originates from the fact that there is a physical positive lower bound on the energy density.

Finally, consider a dilute nuclear matter. Walecka's mean field theory [4] predicts a liquid-gas phase transition somewhere below normal nuclear density. Going below the transition density in the liquid phase, negative pressures can be obtained, similarly to the van der Waals system. However, for finite nuclei the pressure scale is generally shifted in order to get $p = 0$ for normal nuclear density because a nucleus is in mechanical equilibrium with the physical vacuum. Then the pressure becomes negative just under normal nuclear density.

Now, following the philosophy of Denielewicz's approximation [2], and taking the thermal part of the free energy density f from the T^2 expansion of a Fermi gas,

$$f = -\alpha m \hbar^{-2} n^{1/3} T^2 \quad ; \qquad \alpha = \frac{1}{2}\left(\frac{\pi}{3}\right)^{2/3} \quad . \tag{4.8}$$

Then one gets

$$S = 4\alpha m\hbar^2 V^{2/3} N^{1/3}\left\{E - N\left[W_o + \frac{K}{18 n_o^2}\,\frac{(N-n_oV)^2}{V^2}\right]\right\} \quad . \qquad (4.9)$$

But, if $NW_o + NK/18 < E < NW_o + NK/16$, this function has a maximum at

$$V_o = \frac{N^2K/18}{2(E - NW_o - NK/18)}\left(1 + \sqrt{9 + 144\, W_o/K - 144E/NK}\right) \quad . \qquad (4.10)$$

Now the situation is slightly different from the previous two cases. There is no absolute lower bound for E/V, the limit in Postulate VI does exist, and that postulate fixes the zero point of the pressure scale. The limit $V/E \to \infty$ means infinitely diluted nuclear matter, which state can be reached only asymptotically, and is, of course, in mechanical equilibrium with the physical vacuum. Nevertheless, there is a domain of the extensive parameters V, N and E where S is not a monotonously increasing function of V, so the new part of Postulate III cannot be applied on the system, moreover, according to the dynamical calculations [2], this domain can be reached in experiments. Then the remaining thermodynamical postulates cannot guarantee the positivity of the pressure there. The most fundamental reason of this is the quadratic form of the compression energy in Eq. (4.9), if there are good physical arguments for such a behaviour, then this particular system can exist but it is not a normal system, and then the occurrence of negative pressures seems inevitable.

5. CONCLUSIONS

In thermodynamics the absolute pressure scale is generally borrowed from mechanics. Nevertheless Callen's postulate system determines the pressure scale up to an additive constant. Here we have shown that generally this constant can be uniquely defined by a further postulate

$$\lim_{V/E\to\infty} \frac{\partial S}{\partial V} = 0 \qquad (5.1)$$

in such a way that the pressure scale becomes consistent with the mechanics, and in a true dynamical process the zero point can be reached only asimptotically. There are exotic systems where such a limes does not exist, because the system has a positive minimal energy density, then the pressure scale of such a system is given by a mechanical contact with a normal system, but the thermodynamic postulates do not guarantee the positivity of pressure in the whole domain of the extensive parameters. The situation is analogous to the case of negative absolute temperatures which do exist, occurring when the system has an upper bound for the energy density. Similarly to that case the entropy production is positive semidefinite in a dynamical process.

Thus one can conclude that if in a model system the energy density has a positive lower bound, and the pressure is negative, then this negativity can be a consequence of some fundamental assumption imposing the minimum of the energy density on the system, and the thermodynamics does not rule out these states.

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