Thermodynamical aspects of the Casimir force between real metals at nonzero temperature

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We investigate the thermodynamical aspects of the Casimir effect in the case of plane parallel plates made of real metals. The thermal corrections to the Casimir force between real metals were recently computed by several authors using different approaches based on the Lifshitz formula with diverse results. Both the Drude and plasma models were used to describe a real metal. We calculate the entropy density of photons between metallic plates as a function of the surface separation and temperature. Some of these approaches are demonstrated to lead to negative values of entropy and to nonzero entropy at zero temperature depending on the parameters of the system. The conclusion is that these approaches are in contradiction with the third law of thermodynamics and must be rejected. It is shown that the plasma dielectric function in combination with the unmodified Lifshitz formula is in perfect agreement with the general principles of thermodynamics. As to the Drude dielectric function, the modification of the zero-frequency term of the Lifshitz formula is outlined that not to violate the laws of thermodynamics.

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I. INTRODUCTION

Recent advances in experimental investigation of the Casimir effect (see Refs. [1–10] and the review [11]) have given impetus to extensive theoretical studies of different corrections to the Casimir force. Casimir force arises between two closely spaced neutral bodies due to the existence of zero-point electromagnetic fluctuations. It is one of the rare macroscopic manifestations of quantum phenomena. For this reason, it received widespread attention. Moreover, currently the Casimir effect finds applications in fundamental physics for constraining hypothetical forces predicted by different extensions to the standard model [12–14] and also in nanotechnology [7,8].

Originally the Casimir force was computed between two infinitely large plane parallel plates made of ideal metal [15]. Corrections to this ideal result are caused by the geometrical factors (restricted area of the plates and surface roughness), finite conductivity of the boundary metal and nonzero temperature. Geometrical factors are detailedly examined in the literature (see, e.g., their study in Refs. [16–20] and also in [11]). Corrections caused by the finite conductivity of a metal [21–26] and by nonzero temperature [22,27,28], when considered separately, also received much attention and wholly satisfactory results were obtained (see also [11]).

For experimental purposes the combined effect of different corrections to the Casimir force was found to be of large importance. The effect of surface roughness, combined with any other corrections, can be effectively computed by the method of geometrical averaging [11,19]. So one comes face to face with the problem how to find the combined action of finite conductivity and nonzero temperature onto the Casimir force. At first glance it would seem that there is an easy way to solve this problem. Use could be made of the famous Lifshitz formula [21,29] for the Casimir force at nonzero temperature acting between two dielectric semispaces by the substitution of the dielectric permittivity function describing real metals (on the basis of the plasma model, Drude model or optical tabulated data for the complex refractive index). This was done recently by different authors [30–38] and unexpectedly led to conflicting results.

In Refs. [32,33,35] the corrections to the Casimir force due to the combined effect of the finite conductivity and nonzero temperature were calculated in the framework of the Lifshitz formula and of the free electron plasma model. The obtained results are in agreement. Temperature corrections are positive and smoothly transform to those for an ideal metal in the limit of infinite plasma frequency.

In Refs. [34,36] the Drude dielectric function was substituted into the Lifshitz formula. The temperature corrections to the Casimir force were found to be negative at small space separations between the plates. The asymptotic values of the Casimir force at high temperature (large separations) were found to be two times smaller than for ideal metal

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irrespective of how high the conductivity of real metal is. Thus, the results of \[30,31\] do not convert smoothly to the results, given by the plasma model, when the relaxation goes to zero and also to the results, found for an ideal metal, when the plasma frequency goes to infinity. So extraordinary properties of the obtained results were attempted to explain in \[30,31\] by the principal role of nonzero relaxation. Mathematically these properties are caused by the zero value of the reflection coefficient at zero frequency as given by the Lifshitz formula for photons with perpendicular polarization in the framework of the Drude model.

In Refs. \[37,38\] both the plasma and the Drude models were used supplemented by the special prescription modifying the zero-frequency term of the Lifshitz formula in the same way as was done in Ref. \[27\] for the case of an ideal metal. As a result, large temperature corrections arise to the Casimir force at small separations that are linear in temperature. At large separations (high temperatures), asymptotic of the Casimir force in \[37,38\] do not demonstrate any finite conductivity correction starting from a separation of several micrometers.

As explained in Refs. \[34,35\], actually the Drude model is outside of the application range of the Lifshitz formula and, specifically, the zero-frequency term of this formula must be modified in an appropriate way in order to incorporate the dissipative media. This was demonstrated on the basis of a new derivation of the Lifshitz formula \[11\] in the framework of quantum field theory in Matsubara formulation. In Ref. \[11\] the new prescription for the zero-frequency term of the Lifshitz formula was proposed which is not subject to the above-mentioned disadvantages (see also \[36\]). Discussions regarding the correct description of the thermal Casimir force between real metals are, however, being continued (see recent Comments \[39,40\] and Replies \[41,42\] supporting just the opposite points of view). The necessity to conclusively resolve a problem is apparent when it is considered that the experiment is already nearing the registration of the thermal corrections to the Casimir force.

In the present paper we analyse the thermal Casimir force between real metals on the basis of the fundamental principles of thermodynamics. Entropy for a system of photons between the realistic metallic plates is calculated. It is shown that in the approach of Refs. \[31,31\], entropy is negative within the separation range where the temperature correction to the Casimir energy density computed in \[30,31\] is negative. It is proved also that both in Refs. \[30,31\] on the one hand, and in \[37,38\] on the other hand the Nernst heat theorem, or the third law of thermodynamics, is violated. Thus, the approaches of Refs. \[30,31,37,38\] are unacceptable from the thermodynamical point of view. As for the results of Refs. \[32,33,35,36\] (for plasma model) and Refs. \[34,35\] (for Drude model), they are shown to be in agreement with the general principles of thermodynamics.

This paper is organized as follows. In Sec. II the general expression for the entropy of a system of photons between metallic plates is presented. Sec. III contains the computational results for the entropy in the framework of the Drude model using different approaches. In Sec. IV the analogical results obtained in the framework of the plasma model are given. In Sec. V the reader finds conclusions and discussion.

II. ENTROPY FOR PHOTONS BETWEEN PLATES MADE OF REAL METAL

We consider two plane parallel plates made of real metal which are in thermal equilibrium with a heat reservoir at some nonzero temperature $T$. Let $a$ be the space separation between plates. The modern derivation of the free energy per unit area for the system under consideration is based on quantum field theory in the Matsubara formulation and $\zeta$-regularization method. The result is \[11\]

$$F_E(a, T) = \frac{k_B T}{4\pi} \sum_{l=\pm \infty} \int_{0}^{\infty} k_{\perp} dk_{\perp}$$

\begin{equation}
\times \left\{ \ln \left[ 1 - r'_{||}(\xi_l, k_{\perp}) e^{-2aq_{||}} \right] + \ln \left[ 1 - r'_{\perp}(\xi_l, k_{\perp}) e^{-2aq_{\perp}} \right] \right\},
\end{equation}

where

$$r'_{||}(\xi_l, k_{\perp}) = \left[ \frac{\epsilon(i\xi_l)q_{||} + k_{||}}{\epsilon(i\xi_l)q_{||} - k_{||}} \right]^{2}, \quad r'_{\perp}(\xi_l, k_{\perp}) = \left( \frac{q_{\perp} - k_{\perp}}{q_{\perp} + k_{\perp}} \right)^{2}$$

with $q_{||} = (\xi_l^2/c^2 + k_{\perp}^2)^{1/2}$, $k_{||} = [\epsilon(i\xi_l)\xi_l^2/c^2 + k_{\perp}^2]^{1/2}$ are the reflection coefficients for the modes corresponding to two different polarizations. Here $\epsilon$ is the frequency dependent dielectric permittivity of a plate material computed along imaginary frequency axis at discrete Matsubara frequencies $\xi_l = 2\pi l k_B T / h$ with $l = \ldots -2, -1, 0, 1, 2, \ldots$, $k_B$ is the Boltzmann constant, and $k_{\perp}$ is the modulus of the wave vector component in the plane of the plates.
The result \(\text{(1)}\) is obtained by the solution of a one-dimensional scattering problem on the axis perpendicular to the plates. In fact, an electromagnetic wave which is coming from the left in one semispace is scattered on the vacuum gap between semispaces and there are reflected and transmitted waves (see Refs. 11,34,35 for details).

It is important to keep in mind that the scattering problem leading to Eqs. \(\text{(1)}, \text{(4)}\) has the definite solution only under the requirement that

\[
\lim_{\xi \to 0} \xi^2 \varepsilon(i\xi) = C \neq 0. \quad (3)
\]

If this is not the case (like for metals described by the Drude model or for dielectrics, see the next section) some additional conditions must be used to fix a solution of the scattering problem at zero frequency. As an example, for dielectrics the results \(\text{(1)}, \text{(3)}\) are restated including the zero-frequency contribution by using the unitarity condition and dispersion relation. However, as to the case of the Drude model, describing a medium with dissipation, the unitarity condition is not applicable, and, therefore, a solution of the scattering problem at zero frequency remains indefinite. Due to this fact, metals described by the Drude model are outside of the application range of formulas \(\text{(1)}, \text{(4)}\) for the Casimir free energy density at nonzero temperature. The special prescription concerning the zero-frequency term of Eq. \(\text{(1)}\) must be introduced in order that the dissipative media could be described on the basis of this equation. This prescription must be in accordance with the laws of thermodynamics and other general physical requirements.

It is easily seen that Eqs. \(\text{(1)}, \text{(4)}\) lead to the famous Lifshitz formula \(21,22\) for thermal Casimir force between two semispaces which is obtained as \(F(a,T) = -\partial F_E(a,T)/\partial a\). Thus we arrived at the conclusion that the Drude metals are outside of the application range of the Lifshitz formula at nonzero temperature and a special prescription is needed in order to describe them in a consistent way.

In the limit of zero temperature, the Casimir energy density of the zero-point electromagnetic oscillations is reobtained from Eq. \(\text{(1)}\) as

\[
E(a) = \frac{\hbar}{4\pi^2} \int_0^\infty d\xi \int_0^\infty k_\perp dk_\perp \left\{ \ln \left[ 1 - r_\perp^2(\xi, k_\perp) e^{-2aq}\right] + \ln \left[ 1 - r_\perp^2(\xi, k_\perp) e^{-2aq}\right] \right\}. \quad (4)
\]

From \(\text{(1)}\) the Lifshitz formula for the Casimir force at zero temperature is obtained \(F(a) = -\partial E(a)/\partial a\). It is a nontrivial result that the Lifshitz formula at zero temperature is applicable for nondissipative as well as for dissipative media. This was demonstrated in Ref. 34 (see also 23) through the consideration of a supplementary electrodynamic problem and is explained by the fact that the only point \(\xi = 0\) which gives an important contribution to the discrete sum \(\text{(1)}\) does not contribute to the integral \(\text{(4)}\).

Note that the generally accepted terminology “the Casimir energy density and force at zero temperature” is of some ambiguity. It is really correct in the sense that the sum of the zero-point energies (not the free energies) is computed. This terminology, however, disregards the fact that there is a significant thermal dependence of the energy density and force through the thermal dependence of the dielectric permittivity (see the next section). Because of this, when one calculates the Casimir energy density at, say, \(T = 300\, \text{K}\), the value of \(\varepsilon(i\xi, T)\) is substituted into Eq. \(\text{(1)}\), not \(\varepsilon(i\xi, T = 0)\) (see, e.g., Refs. 23,26,21,22). Thus, instead of \(E(a)\), a more exact notation for the quantity \(\text{(1)}\) would be \(E_T(a)\).

If we multiply \(\text{(1)}\) or \(\text{(4)}\) by \(2\pi R\), where \(R \gg a\) is a radius of a sphere at a separation \(a\) from the semispace, one obtains the Casimir force in the configuration of a sphere near a plate at a temperature \(T\), or at zero temperature, respectively \(\text{(1)}\).

According to thermodynamics, the entropy per unit area of the system under consideration is

\[
S(a,T) = \frac{1}{T} \left[ E_T(a) - F_E(a,T) \right], \quad (5)
\]

where \(F_E(a,T)\) is given by Eq. \(\text{(1)}\) and \(E_T(a) \equiv E(a)\) from Eq. \(\text{(1)}\). In the next sections entropy is calculated for the plates made of real metal as described by the Drude or plasma model dielectric functions. In doing so, special attention is paid to the zero-frequency term \((l = 0)\) in Eq. \(\text{(1)}\) and to the fulfilment of Eq. \(\text{(1)}\).

III. ENTROPY IN THE CASE OF METALLIC PLATES DESCRIBED BY THE DRUDE MODEL

It is common knowledge that the Drude dielectric function
\[ \varepsilon_D(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \]  

(6)

where \( \omega_p \) is the plasma frequency and \( \gamma \ll \omega_p \) is the relaxation frequency, gives a good approximation of the dielectric properties for some metals, e.g., for aluminum. This approximation was widely used in combination with the Lifshitz formula \( (\text{3}) \) to calculate the finite conductivity corrections to the Casimir force at zero temperature \( (\text{11,22,26}) \). To do so the Drude dielectric function along the imaginary frequency axis was considered

\[ \varepsilon_D(i\xi) = 1 + \frac{\omega_p^2}{\xi(\xi + \gamma)}. \]  

(7)

Before we proceed further, we note that the dielectric function \( (\text{3}) \) violates the requirement \( (\text{2}) \) for any nonzero value of the relaxation frequency \( \gamma \). Due to this, as discussed in the previous section, the Drude metals are outside of the application range of the Lifshitz formula \( (\text{3}) \) at nonzero temperature with an unmodified zero-frequency term. If, nevertheless, one substitutes Eq. \( (\text{7}) \) into Eq. \( (\text{1}) \), as was done, e.g., in Refs. \( (\text{6,30,31}) \), several questionable results follow which are in contradiction with the limiting cases of metal described by the plasma model (see the next section) and of an ideal metal (see Introduction and a detailed discussion in Refs. \( (\text{34–36}) \)).

Using the dielectric function of Eq. \( (\text{7}) \), the values of reflection coefficients \( (\text{2}) \) at zero frequency are the following

\[ r_\parallel^2(0,k_{\perp}) = 1, \quad r_\perp^2(0,k_{\perp}) = 0. \]  

(8)

From the formal point of view, some troubles are connected with the second of Eqs. \( (\text{5}) \) because for an ideal metal \( r_\perp^2(0,k_{\perp}) = 1 \).

In order to present the crucial argument against the substitution of the Drude dielectric function \( (\text{3}) \) into the unmodified Lifshitz formula \( (\text{3}) \) at nonzero temperature, we calculate the entropy per unit area given by Eq. \( (\text{5}) \) in the framework of the Drude model. Thus, as an example, consider \( \mid \text{Al} \) plates with the parameters \( (\text{45}) \)

\[ \omega_p \approx 12.5 \text{ eV} \approx 1.9 \times 10^{16} \text{ rad/s}, \]

\[ \gamma \approx 0.063 \text{ eV} \approx 9.6 \times 10^{13} \text{ rad/s}. \]  

(9)

In Fig. 1 the computational results for the entropy are presented at \( T = 300 \text{ K} \) as a function of the separation between the plates. Note that the plasma frequency practically does not depend on temperature. As to the value of the relaxation frequency from Eq. \( (\text{9}) \), it is given for the temperature under consideration. It is seen from the figure that the entropy is negative within a wide separation range that it not acceptable from a thermodynamical point of view. The separation interval \( 0 < a < 4.1 \mu \text{m} \), where the entropy is negative, coincides with the interval where the negative temperature corrections arise in the approach used in \( (\text{31}) \) (see the detailed discussion in \( (\text{34}) \)). Negative temperature corrections are in conflict with the evident physical arguments (with increase of temperature the number of photons in the modes and thereby force modulus should increase). Here we show that they are also in contradiction with the general physical principles.

As noted in the Introduction, except of the immediate application of the Lifshitz formula in combination with the Drude model \( (\text{6,31}) \), different prescriptions were proposed in literature modifying the zero-frequency term of this formula in the case of real metals. In \( (\text{23,35}) \) it was postulated that

\[ r_\parallel^2(0,k_{\perp}) = r_\perp^2(0,k_{\perp}) = 1, \]  

(10)

as in the case of an ideal metal. This prescription was criticized on physical grounds in \( (\text{34}) \).

In Ref. \( (\text{34}) \) the other prescription was proposed which is the generalization of the prescription of Ref. \( (\text{22}) \), formulated for an ideal metal. According to \( (\text{34}) \) in the framework of the Drude model the reflection coefficients at zero frequency are

\[ r_\parallel^2(0,k_{\perp}) = 1, \quad r_\perp^2(0,k_{\perp}) = \left( \frac{ck_{\perp} - \sqrt{\omega_p^2 + c^2k_{\perp}^2}}{c + \sqrt{\omega_p^2 + c^2k_{\perp}^2}} \right)^2. \]  

(11)

As shown in \( (\text{34}) \), prescription \( (\text{11}) \) leads to wholly satisfactory results.

In order to test all the above approaches for conformity to the general principles of thermodynamics, we find the dependence of the entropy \( (\text{3}) \) on temperature at some fixed plate separation, say, \( a = 2 \mu \text{m} \). To accomplish this, one should take into consideration that except of the evident dependence of Eqs. \( (\text{1}) \) and \( (\text{3}) \) on temperature there is the
The aforementioned significant thermal dependence of $\varepsilon_p$ given by Eq. (7) through the relaxation parameter $\gamma = \gamma(T)$ (coinciding with the thermal dependence of resistance). The dependence $\gamma(T)$ is linear at temperatures higher than $0.25T^*$, where $T^*$ is the Debye temperature ($T^* = 428$ K for Al [46]). At lowest temperatures $\gamma(T)$ follows the power law $T^n$ ($n = 2 - 5$ depending on the metal). The complete dependence of the nondimensional normalized quantity $\tilde{\gamma}(T) \equiv 2\alpha \gamma(T)/c$ on the temperature is plotted in Fig. 2 by the use of tabulated data for Al [46] (here we neglect the small residual resistivity caused by the scattering of electron waves by static defects that is outside of the frameworks of the Drude model [47]).

Now we are in a position to calculate the dependence of entropy on temperature for all the above approaches. Calculation was performed using Eq. (8) and also Eqs. (1), (4), (6) and Fig. 2. The results are presented in Fig. 3. The long-dashed curve is obtained on the basis of the Lifshitz formula with an unmodified zero-frequency term (i.e., Eq. (8) was used for the reflection coefficients at zero frequency). Remind that this approach was exploited in Refs. [30,31]. The short-dashed curve is calculated with the modification of the zero-frequency term of the Lifshitz formula according with Eq. (10) suggested in Ref. [34]. Note that all the above approaches differ by the value of the zero-frequency term only for perpendicular polarization.

As is quite clear from Fig. 3, for both long-dashed and short-dashed curves the values of entropy at zero temperature are not equal to zero. In the approach used in [30,31] $S_1(0) = -0.5$ MeV m$^{-2}$ K$^{-1}$, and in the approach used in [37,38] $S_2(0) = 0.016$ MeV m$^{-2}$ K$^{-1}$. In both cases the value of $S(0)$ depends on the parameters of the system under consideration (like the separation between the plates and the plasma frequency) that is in manifest contradiction with the third law of thermodynamics (the Nernst heat theorem [18,19]). It is notable that the entropy density given by the long-dashed curve is negative in a wide temperature range (compare with Fig. 1 where the result at a fixed temperature is presented). It is easily shown that the values of entropy density at zero temperature, given by the dashed curves, are related by

$$
S_2(0) - S_1(0) = \frac{k_B \zeta(3)}{16\pi a^2},
$$

where $\zeta(3)$ is the Riemann zeta function. The right-hand side of Eq. (12) is equal to one-half of the coefficient near temperature in the zero-frequency term of the Lifshitz formula for an ideal metal. This is because in [37,38] the same values (10) for the reflection coefficients at zero frequency were postulated as for an ideal metal, whereas in [30,31], according to [8], one-half of the result for an ideal metal was used. In fact the correct result for a real metal lies in between of these two possibilities.

Contrary to the dashed curves, for the solid curve (approach of Ref. [34]), $S(0) = 0$ and therefore, in accordance with the laws of thermodynamics.

**IV. ENTROPY IN THE CASE OF METALLIC PLATES DESCRIBED BY THE PLASMA MODEL**

For the free-electron plasma model the dependence of dielectric function on the frequency is given by

$$
\varepsilon_p(\omega) = 1 - \frac{\omega_p^2}{\omega_t^2}, \quad \varepsilon_p(i\xi) = 1 + \frac{\omega_p^2}{\xi^2}.
$$

(13)

This dependence was widely used to calculate the finite conductivity corrections to the Casimir force at the separations of order 1 $\mu$m [21,23]. In Refs. [32,33] it was applied to compute the effect of nonzero temperature and finite conductivity in the framework of the Lifshitz formula [1]. Note that the plasma dielectric function practically does not depend on temperature.

The preference for the plasma model as compared with the Drude one is the fulfilment of condition (3) with the dielectric function (13). As a consequence, the scattering problem underlying the Lifshitz theory has a definite solution leading to Eqs. (1), (2), (4) including the zero-frequency contribution. The reflection coefficients (3) at zero frequency in the framework of the plasma model take the form

$$
\tilde{r}^2_1(0, k_\perp) = 1, \quad \tilde{r}^2_\perp(0, k_\perp) = \frac{c k_\perp - \sqrt{\omega_p^2 + c^2 k_\perp^2}}{c k_\perp + \sqrt{\omega_p^2 + c^2 k_\perp^2}}. \quad (14)
$$

Note that Eq. (14) can be obtained from Eq. (11) when the relaxation frequency goes to zero. Because of this, in the approach of [34] the results for the plasma model are obtainable from the results for the Drude model in a limiting
case \( \gamma \to 0 \) (the results obtained in [30,31] by the use of the Drude model on the basis of Eq. (8) have no smooth connection with a plasma model approach; the plasma model by itself is not considered in [30,31]). In the alternative approach [37,38], as distinct from both [32,35] and [30,31], the conditions (10) are postulated in the framework of both Drude and plasma models.

Now let us find the dependence of the entropy density on temperature in the framework of the plasma model on the basis of different approaches. As an example, Al plates are used once more at a separation \( a = 2 \mu m \). The value of the plasma frequency for Al is given by Eq. (1). Calculations were performed using Eqs. (1), (4), (6), (7) and (13). The results are presented in Fig. 4. The dashed curve is obtained in the framework of Refs. [37,38] using prescription (14). The solid curve is calculated on the basis of Refs. [32,35] with no modification of the Lifshitz formula, i.e. with the zero-frequency reflection coefficients (13).

As is obvious from Fig. 4, for the dashed curve the value of entropy at zero temperature \( \tilde{S}(0) = S_2(0) = 0.016 \text{MeV m}^{-2} \text{K}^{-1} \) and is not equal to zero. It depends on the parameters of the system that is in contradiction with the third law of thermodynamics. In contrast to this, for the solid curve obtained on the basis of the fundamental Lifshitz formula, \( S(0) = 0 \) as it must be from the third law of thermodynamics.

In the framework of the plasma model it is not difficult to obtain the analytical expression for the entropy at low temperatures \( k_B T \ll k_B T_{eff} = \hbar c/(2a) \). For this purpose the perturbation expansion of the Casimir energy and free energy in powers of two small parameters \( \delta_0/a = c/(\omega_0 \lambda_p) \) and \( T/T_{eff} \) can be used (see Refs. [24,33,35] where these expansions are presented in details; they are applicable for separations \( a \geq \lambda_p = 2 \pi c/\omega_p \) where \( \lambda_p \) is the effective plasma wavelength). Substituting the mentioned perturbation expansions into Eq. (5), one obtains

\[
S(a, T) = \frac{k_B \zeta(3)}{8 \pi a^2} \left( \frac{T}{T_{eff}} \right)^2 \left\{ 1 - \frac{\pi^3 T}{45 \zeta(3) T_{eff}} \right\} - \frac{2 \delta_0}{a} \left[ 1 - \frac{2 \pi^3}{45 \zeta(3)} \frac{T}{T_{eff}} \right].
\]  

Here the terms up to \( (T/T_{eff})^3 \) were included. The powers of \( \delta_0/a \) higher than one are contained only with powers \( (T/T_{eff})^n, n > 3 \). This analytical expression corresponds to the solid curve in Fig.4. It is seen from Eq. (15) that the entropy approaches zero as the second power of temperature in the framework of the unmodified Lifshitz formula.

On the basis of the approach proposed in Refs. [33,35] the perturbation expansion of entropy is given by

\[
\tilde{S}(a, T) = \frac{k_B \zeta(3)}{4 \pi a^2} \frac{\delta_0}{a} \left( 1 - 3 \frac{\delta_0}{a} \right) + S(a, T),
\]  

where \( S(a, T) \) is expressed by Eq. (13). The first contribution in the right-hand side of Eq. (16) is the value of entropy at zero temperature

\[
\tilde{S}(a, 0) = \frac{k_B \zeta(3)}{4 \pi a^2} \frac{\delta_0}{a} \left( 1 - 3 \frac{\delta_0}{a} \right) \neq 0.
\]  

At \( a = 2 \mu m \) one obtains from Eq. (7) the above value of \( S_2(0) \). \( \tilde{S}(a, 0) \) depends on both the separation between the plates \( a \) and the penetration depth of the electromagnetic oscillations into the plate material \( \delta_0 \) in contradiction with the third law of thermodynamics [38,39].

V. CONCLUSION AND DISCUSSION

In the foregoing we have considered the thermodynamical aspects of the Casimir force acting between real metals at nonzero temperature. The necessity of considering these aspects stems from the controversial results obtained by different authors (see Refs. [30,35] and continuing polemic [38,32]. The further importance to this problem is added by the rapid progress in experiment on measuring the Casimir force. At the moment, there is a contradiction between the experimental results of [1] and the theoretical approach of [38,31] which leads to large negative temperature corrections at separation of about 1 \( \mu m \) (see the discussion in [39,32]). On the other hand, the experimental results of [2,3] do not agree with the computations of [37,38] that lead to large (although positive) linear in temperature corrections to the Casimir force at separations of about 100 nm (see [34]).

Bearing in mind that there are many influential factors in so precise experiments, it is highly desirable to offer some decisive theoretical arguments providing a way to give preference to one of the theoretical approaches. As
shown above, thermodynamics gives the possibility to make a selection and to reject the approaches that are not in accordance with the most fundamental physical principles.

In the present paper we calculated the entropy density for photons between two parallel plates made of real metals described by the Drude or plasma models. It is shown that in the approach of Refs. [30,31], based on a direct application of the unmodified Lifshitz formula in the case of Drude metals, entropy takes negative values in a wide range of related parameters. The value of entropy density at zero temperature, as given by the approach of [30,31], is shown to be nonzero and dependent on the parameters of the system under consideration in contradiction with the Nernst heat theorem. These unacceptable properties of entropy confirm the conclusion of Refs. [34,35] that the dissipative metals described by the complex dielectric permittivity of real frequency are outside of the application range of the Lifshitz formula at nonzero temperature. To describe the thermal Casimir force for such metals a special prescription should be adopted modifying the zero-frequency term of the Lifshitz formula.

One prescription of this kind (the same as was proposed in [22] for the case of ideal metal) was suggested in Refs. [37,38]. We show that although the entropy density in the approach of [37,38] is positive, the value of entropy at zero temperature is not equal to zero and depends on the parameters of the system. Thus, this approach is also in contradiction with the third law of thermodynamics.

One more prescription for the zero-frequency term of the Lifshitz formula was proposed in [34]. It is the generalization of the receipt of [22] for the case of real metals. We show that for the prescription suggested in [34], entropy is non-negative at all temperatures and takes zero value at zero temperature. Hence the prescription of Ref. [34] is in agreement with the general principles of thermodynamics.

In this paper we report also the results of the computation of the entropy in the framework of the plasma model. The plasma model does not take dissipation into account. It belongs to the application range of the Lifshitz formula. It is shown that the application of the unmodified Lifshitz formula in combination with the plasma model leads to wholly satisfactory results: the entropy density is positive and takes zero value at zero temperature. The application of the modified Lifshitz formula, as in Refs. [37,38], leads to the violation of the third law of thermodynamics.

To conclude, the approach of Refs. [30,31] on the one hand and of Refs. [37,38] on the other hand must be rejected as they are in contradiction with the general principles of thermodynamics. In the case of the Drude metals only the approach of Ref. [34] fits thermodynamical requirements. It is also in accordance with the present experimental results. As to the case of the plasma metals with no account of dissipation, the unmodified Lifshitz formula is applicable and the results of Refs. [32–36] are in agreement between themselves and with the general principles of thermodynamics.

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FIG. 1. Entropy of photons between Al plates described by the Drude model at $T = 300\, \text{K}$ as a function of space separation computed using the approach of Refs. [30,31].
FIG. 2. Dimensionless relaxation frequency of $Al$ as a function of temperature.
FIG. 3. Entropy of photons between Al plates described by the Drude model at a separation $a = 2 \mu m$ as a function of the temperature. Long-dashed curve was computed using the approach of Refs. [30,31], the short-dashed curve was obtained with the approach of [37,38], and the solid curve using the approach of [34].
FIG. 4. Entropy of photons between Al plates described by the plasma model at a separation $a = 2 \mu$m as a function of the temperature. Dashed curve was computed using the approach of [37,38] and the solid curve was obtained with the approach of [32–36].