Correlation of energy and free energy for the thermal Casimir force between real metals

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The energy of fluctuating electromagnetic field is investigated for the thermal Casimir force acting between parallel plates made of real metal. It is proved that for nondissipative media with temperature independent dielectric permittivity the energy at nonzero temperature comprises of the (renormalized) energies of the zero-point and thermal photons. In this manner photons can be considered as collective elementary excitations of the matter of plates and electromagnetic field. If the dielectric permittivity depends on temperature the energy contains additional terms proportional to the derivatives of \( \varepsilon \) with respect to temperature, and the quasiparticle interpretation of the fluctuating field is not possible. The correlation between energy and free energy is considered. Previous calculations of the Casimir energy in the framework of the Lifshitz formula at zero temperature and optical tabulated data supplemented by the Drude model at room temperature are analysed. It is demonstrated that this quantity is not a good approximation either for the free energy or the energy. A physical interpretation of this hybrid quantity is suggested. The contradictory results in the recent literature on whether the zero-frequency term of the Lifshitz formula for the perpendicular polarized modes has any effective contribution to the physical quantities are discussed. Four main approaches to the resolution of this problem are specified. The precise expressions for entropy of the fluctuating field between plates made of real metal are obtained, which helps to decide between the different approaches. The conclusion is that the Lifshitz formula supplemented by the plasma model and the surface impedance approach are best suited to describe the thermal Casimir force between real metals.

PACS numbers: 12.20.Dc, 42.50.Lc, 65.50.+m

I. INTRODUCTION

The Casimir effect is a rare macroscopic manifestation of the zero-point electromagnetic energy. It results from the alteration of the zero-point spectrum by the material boundaries (see the original Casimir’s paper \( \cite{1} \) and extensive reviews \( \cite{2,3,4,5,6} \)). In recent years considerable attention was paid to the precision measurements of the Casimir force between metallic surfaces \( \cite{7,8,9,10,11,12,13,14,15} \). The results of these measurements were used in Refs. \( \cite{16,17,18,19,20} \) to constrain the hypothetical interactions predicted by many extensions to the Standard Model and also in nanotechnology \( \cite{21} \). This called for new theoretical investigation of the Casimir force with allowance made for the realistic boundary properties, i.e., surface roughness, finite conductivity of a metal and nonzero temperature (see Ref. \( \cite{2} \) for the review). Also the combined effect of these factors has attracted considerable attention.

In this paper we consider the correlation between energy and free energy for the Casimir force acting between two plane parallel plates made of real metal of finite conductivity kept at nonzero temperature. At zero temperature the influence of the finite conductivity of the boundary metal onto the Casimir force was examined in Refs. \( \cite{22,23,24,25} \) on the basis of the Lifshitz theory using the optical tabulated data supplemented by the Drude model. In this approach the Casimir energy was represented by an integral with respect to continuous frequency, as it is at zero temperature. However, the optical tabulated data and the value of the relaxation parameter of the Drude model at \( T = 300 \) K were substituted, which are actually temperature dependent. By this means, in fact, some hybrid quantity was computed, which is different from both energy and free energy, with no clear relevance to either of them. When it is considered that the Casimir energy between two plates is generally used to calculate the Casimir force in the experimental configuration of a sphere (spherical lens) above a plate, the resolution of this issue is of great interest. Below is shown the relationship between energy, free energy and a quantity computed in Refs. \( \cite{22,23,24,25} \).

Investigation of the correlation between energy and free energy for the thermal Casimir force has also assumed great importance in connection with the contradictory results obtained by different authors when applying the Lifshitz theory to real metals \( \cite{26,27,28,29,30,31,32,33,34,35,36,37,38,39} \). The contradictions arise on whether or not the zero-frequency term of the Lifshitz formula for the perpendicular polarized modes of electromagnetic field contribute to physical quantities. There are four main approaches to the resolution of this issue in the recent literature.

a) According to Refs. \( \cite{26,30} \) based on the immediate application of the unmodified Lifshitz formula, the zero-frequency term of this formula for the perpendicular polarized modes is equal to zero in the case of real metals described by the Drude model (remind the reader that for ideal metals the reflection coefficients for both polarizations are equal to unity at zero frequency, and hence the zero-frequency term for both modes is not equal to zero). This approach leads to the conclusion that thermal corrections to the Casimir force are large, negative, and linear in
temperature at small separations, and the asymptotic Casimir force between real metals at large separations is two times smaller than for the case of an ideal metal (with no regard for the particular value of the conductivity) [32].

b) From the standpoint of Refs. [25,26], the perpendicular polarized modes give a nonzero contribution at zero frequency. To find it, a special modification of the zero-frequency term of the Lifshitz formula was proposed (found by analogy with the prescription of Ref. [23] for an ideal metal but not coinciding with it).

c) According to Refs. [31,32], the perpendicular polarized modes also give a nonzero contribution at zero frequency. For real metals it is, however, the same as for ideal metal, i.e., the reflection coefficients for both modes are equal to unity at zero frequency. What this means is for real metals the same modification of the zero-frequency term of the Lifshitz formula is made as for ideal metals [34]. This approach leads to linear (although positive) thermal corrections to the Casimir force at small separations and to the absence of any finite conductivity corrections for real metals starting from moderate separations of several micrometers regardless of metal quality [32].

d) Finally, according to the approach of Refs. [27,28,29] both modes with the parallel and perpendicular polarizations do contribute to the zero-frequency term and this contribution can be calculated by the substitution of the plasma model dielectric function into the unmodified Lifshitz formula. The same conclusion is obtained in Ref. [33] on the basis of the surface impedance approach.

Thus, at the moment there is no agreement in the theoretical literature as to the description of the thermal Casimir force between real metals. To gain a more complete understanding of the present state of affairs, in Ref. [34] the thermodynamical argument was exploited. According to Ref. [34], the approaches a) and c) do not conform to the requirements of thermodynamics as they lead to the negative values of entropy and violation of the Nernst heat theorem. Although the qualitative conclusions of [34] are quite correct, the quantitative calculations are incomplete as they do not take into account the entropy of real photons. The precise expressions for the energy and free energy of the fluctuating electromagnetic field found below are used to obtain the quantitative behavior of entropy as a function of surface separation distance and temperature. The obtained results confirm the conclusion of Ref. [34] that the approaches a) and c) are not compatible with thermodynamics. They also give the possibility to compare the approaches b) and d) in order to decide between them.

The paper is organized as follows. In Sec. II the main notations are introduced and the case of nondissipative condensed media separated by a gap is considered, with the media described by a temperature independent dielectric permittivity. It is proved that in this situation one can introduce photons as quasiparticles due to the collective elementary excitations of condensed matter and electromagnetic field. As a consequence, the energy at temperature $T$ defined via the derivative of the free energy with respect to $T$ comprises of the (renormalized) energies of the zero-point and thermal photons. In Sec. III the energy and free energy of the fluctuating electromagnetic field are considered on the basis of the Lifshitz theory and the plasma model. In Sec. IV the applicability of the Drude model for the calculation of the thermal Casimir force is discussed. The energy and free energy are found in the case of a metal described by the Drude model. The alternative approaches to this problem available in literature are analysed and compared. The physical sense of the energy at temperature $T$ appears to be more complicated than in the case of the plasma model. It is shown that energy contains additional terms depending on the derivatives of the dielectric permittivity with respect to temperature. In Sec. V the entropy for the thermal Casimir force acting between real metals is calculated precisely for both plasma and Drude dielectric functions. Sec. VI contains conclusions and discussion.

II. PHOTONS BETWEEN PLATES AS ELEMENTARY EXCITATIONS

We consider the configuration of two semispaces (thick plates) with frequency-dependent dielectric permittivity $\varepsilon(\omega)$ restricted by parallel planes and separated by an empty space with distance $a$ between them at a temperature $T$. This is a system in thermal equilibrium. The free energy per unit area is given by the well known Lifshitz formula [22,28,29]

$$F_E(a, T) = \frac{k_B T}{4\pi} \sum_{l=-\infty}^{\infty} \int_0^\infty k_\perp dk_\perp \left[ \ln \Delta||_l(\xi_l, k_\perp) + \ln \Delta_\perp(\xi_l, k_\perp) \right].$$  \hspace{1cm} (1)

Here $\Delta_{||,\perp}(\omega, k_\perp)$ are the quantities having zero values on the photon eigenfrequencies permitted between the plates by the boundary conditions (indices $||, \perp$ label two independent polarizations, and $k_\perp$ is the modulus of a wave vector in the plane of plates)

$$\Delta_{||,\perp}(\omega_{k_\perp,n}, k_\perp) = 0.$$  \hspace{1cm} (2)

$$\varepsilon$$
They can be expressed in terms of reflection coefficients on the imaginary frequency axis

\[ \Delta_{\parallel,\perp}(\xi_l, k_{\perp}) = 1 - r_{\parallel,\perp}^2(\xi_l, k_{\perp})e^{-2\alpha q_l}, \]  

(3)

where

\[ r_{\parallel}^2(\xi_l, k_{\perp}) = \left[ \frac{\xi_l q_l - k_{\perp}}{\xi_l q_l + k_{\perp}} \right]^2, \quad r_{\perp}^2(\xi_l, k_{\perp}) = \left( \frac{q_l - k_{\perp}}{q_l + k_{\perp}} \right)^2 \]

(4)

with the notations

\[ q_l \equiv \sqrt{\frac{\xi_l^2}{c^2} + k_{\perp}^2}, \quad k_{\perp} \equiv \sqrt{\frac{\xi_l^2}{c^2} + k_{\perp}^2}. \]

(5)

In Eq. (1) \( k_B \) is the Boltzmann constant and \( \xi_l = 2\pi l k_B T/\hbar \), where \( l = 0, \pm 1, \pm 2, \ldots \), are the Matsubara frequencies. As seen from Eq. (4), the quantities \( \Delta_{\parallel,\perp} \) are normalized in such a way that the free energy (1) tends to zero for the infinitely remote plates (\( a \to \infty \)). The details of the renormalization procedure can be found in Refs. [6,25].

In this section we consider nondissipative media, which is to say that \( \varepsilon \) does not depend on temperature. Both conditions are satisfied, e.g., for metals described by the plasma model or for dielectrics with a constant dielectric permittivity (the case of dissipative media is considered in Secs. IV, V). Under these conditions we find the simple quasiparticle interpretation for photons between plates and the expression for the energy of the fluctuating field at a temperature \( T \).

According to thermodynamics, energy at arbitrary temperature is given by

\[ E(a, T) = -T^2 \frac{\partial}{\partial T} \frac{F_E(a, T)}{T}, \]

(6)

where the free energy is defined in Eq. (1).

Taking into account that the term of Eq. (1) with \( l = 0 \) is linear in temperature and the quantities \( \Delta_{\parallel,\perp} \) are even functions of \( l \) one obtains

\[ E(a, T) = -\frac{k_B T^2}{2\pi} \sum_{l=1}^{\infty} \int_0^\infty k_{\perp} dk_{\perp} \frac{\partial}{\partial T} \left[ \ln \Delta_{\parallel}(\xi_l, k_{\perp}) + \ln \Delta_{\perp}(\xi_l, k_{\perp}) \right]. \]

(7)

Let us next use that \( \Delta_{\parallel,\perp} \) depend on temperature through the Matsubara frequencies only, so that \( \partial/\partial T = (\xi_l/T)\partial/\partial \xi_l \). Thus, energy per unit area is given by

\[ E(a, T) = -\frac{k_B T}{2\pi} \sum_{l=1}^{\infty} \int_0^\infty k_{\perp} dk_{\perp} \left[ \ln \Delta_{\parallel}(\xi_l, k_{\perp}) + \ln \Delta_{\perp}(\xi_l, k_{\perp}) \right]. \]

(8)

We consider now the interpretation of energy at temperature \( T \) in terms of elementary excitations. In the case of the nondissipative media under consideration the photon eigenfrequencies are real and the nonrenormalized energy of equilibrium fluctuating electromagnetic field in the system comprises of the energy of zero-point fluctuations and Planck’s protons \[39\]

\[ E_{nr}(a, T) = \hbar \int_0^\infty \frac{k_{\perp} dk_{\perp}}{2\pi} \sum_n \left\{ \omega_{k_{\perp},n}^{\parallel} \left[ \frac{1}{\sqrt{1 + \frac{\omega_{k_{\perp},n}}{\hbar k_{\perp}}} - 1} \right] + \omega_{k_{\perp},n}^{\perp} \left[ \frac{1}{\sqrt{1 + \frac{\omega_{k_{\perp},n}}{\hbar k_{\perp}}} - 1} \right] \right\}. \]

(9)

Identically, Eq. (9) can be rearranged to give

\[ E_{nr}(a, T) = \frac{\hbar}{2} \int_0^\infty \frac{k_{\perp} dk_{\perp}}{2\pi} \sum_n \left( \omega_{k_{\perp},n}^{\parallel} \coth \frac{\omega_{k_{\perp},n}}{2k_B T} + \omega_{k_{\perp},n}^{\perp} \coth \frac{\omega_{k_{\perp},n}}{2k_B T} \right). \]

(10)

This quantity is evidently infinite. The renormalized value of the sum over the eigenfrequencies \( \omega_{k_{\perp},n}^{\parallel,\perp} \) can be calculated by the use of the argument theorem \[2,3,6,25,40\],

\[ \sum_n \left( \omega_{k_{\perp},n}^{\parallel} \coth \frac{\hbar \omega_{k_{\perp},n}^{\parallel}}{2k_B T} + \omega_{k_{\perp},n}^{\perp} \coth \frac{\hbar \omega_{k_{\perp},n}^{\perp}}{2k_B T} \right) = \frac{1}{2\pi i} \int_C \omega \coth \frac{\hbar \omega}{2k_B T} d \left[ \ln \Delta_{\parallel}(\omega, k_{\perp}) + \ln \Delta_{\perp}(\omega, k_{\perp}) \right], \]

(11)
where the integration path $C$ in the plane of complex $\omega$ is shown in Fig. 1, and the normalized quantities $\Delta_{\parallel,\perp}$, having zero values on eigenfrequencies, were substituted defined by Eqs. (3)–(5), with $\xi_l$ changed by $-i\omega$. Note that the function $\omega \coth [\hbar \omega/(2k_B T)]$ has poles at the imaginary frequencies $\omega_l = i\xi_l$, $l = \pm 1, \pm 2, \ldots$, where $\xi_l$ are the Matsubara frequencies (it is, however, regular at $\omega_0 = 0$). Because of this, the integration along the imaginary axis involves semicircles about these poles. Integration along a semicircle, whose radius extends to infinity, makes zero contribution to the right-hand side of Eq. (11). As a result Eq. (11) leads to

$$\sum_n \left( \frac{\omega_{\|,n}}{2k_BT} \coth \frac{\hbar \omega_{\|,n}}{2k_BT} + \omega_{\perp,n} \coth \frac{\hbar \omega_{\perp,n}}{2k_BT} \right) = \frac{i}{2\pi} \int_{-\infty}^{\infty} \xi \coth \frac{\hbar \xi}{2k_BT} d \left[ \ln \Delta_{\parallel}(\xi, k_{\perp}) + \ln \Delta_{\perp}(\xi, k_{\perp}) \right]$$

$$- \sum_{l=1}^{\infty} \text{Res} \left[ \omega \coth \frac{\hbar \omega}{2k_BT} \frac{\Delta'_{\|}(\omega, k_{\perp})}{\Delta_{\|}(\omega, k_{\perp})}, i\xi_l \right] - \sum_{l=1}^{\infty} \text{Res} \left[ \omega \coth \frac{\hbar \omega}{2k_BT} \frac{\Delta'_{\perp}(\omega, k_{\perp})}{\Delta_{\perp}(\omega, k_{\perp})}, i\xi_l \right]$$

$$= -\frac{2k_BT}{\hbar} \sum_{l=1}^{\infty} \xi_l \left[ \frac{1}{\Delta_{\|}(\xi_l, k_{\perp})} \frac{\partial \Delta_{\|}(\xi_l, k_{\perp})}{\partial \xi_l} + \frac{1}{\Delta_{\perp}(\xi_l, k_{\perp})} \frac{\partial \Delta_{\perp}(\xi_l, k_{\perp})}{\partial \xi_l} \right].$$

Here prime denotes the derivative with respect to $\omega$ and we took into account that $\Delta_{\parallel,\perp}$ are even functions of $\omega$, so that their derivatives are odd ones. This property leads also to the zero value of the seemingly pure imaginary integral in the right-hand side of Eq. (12).

Substituting the right-hand side of Eq. (12) into Eq. (11) instead of a nonrenormalized sum, we obtain the renormalized energy at a temperature $T$ coinciding with Eq. (8) derived from the thermodynamical definition (1). In such a manner we have proved that at certain conditions the thermodynamical energy at equilibrium is given by the additive sum of the contributions from the zero-point fluctuations and Planck’s photons. The renormalization of both quantities reduces to the subtraction of the contribution of a free space with no plates. As a consequence, in the absence of dissipation, photons between plates can be considered as some kind of quasiparticle excitations in the system of the electromagnetic field interacting with the matter of plates. The simple example of this situation is given by metals described by the plasma model.

### III. ENERGY AND FREE ENERGY FOR THE THERMAL CASIMIR FORCE IN THE FRAMEWORK OF THE PLASMA MODEL

The considerations of the previous section can be illustrated by the dielectric function of the plasma model

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

where $\omega_p$ is the plasma frequency. This dielectric function is real and its parameter does not depend on temperature. The use of the plasma model to calculate the thermal Casimir force corresponds to the approach d) described in the introduction. The free electron plasma model works well for frequencies of visible light and infrared optics. It is common knowledge that the dominant contribution to the Casimir effect comes from the range around the characteristic frequency $\omega_c = c/(2a)$. Thus the plasma model is applicable in the $a$-range from a few tens of nanometers to around a hundred micrometers.

For the sake of convenience, we introduce the dimensionless variables

$$\tilde{\xi} = \frac{2a\xi}{c}, \quad y^2 = 4a^2 \left( k_{\perp}^2 + \frac{\xi^2}{c^2} \right)$$

in terms of which the plasma dielectric function takes the form

$$\varepsilon(i\xi) = 1 + \frac{\omega_p^2}{\xi^2}, \quad \tilde{\omega}_p = \frac{2a\omega_p}{c}.$$

In terms of the variables $\tilde{\xi}$, $y$ the Lifshitz formula (1) can be rewritten as

$$F_E(a, T) = \frac{k_BT}{16\pi a^2} \sum_{l=-\infty}^{\infty} \int_{|\tilde{\xi}|}^{\infty} y dy \left[ \ln \Delta_{\|}(\tilde{\xi}, y) + \ln \Delta_{\perp}(\tilde{\xi}, y) \right],$$

where
where

$$\Delta_{\parallel,\perp}(\xi, y) = 1 - r_{\parallel,\perp}^2(\xi, y) e^{-y}$$

and the reflection coefficients are

$$r_{\parallel}^2(\xi, y) = \left\{ \begin{array}{ll}
\frac{\varepsilon(i\xi) - \sqrt{[\varepsilon(i\xi) - 1] \xi^2 + y^2}}{\varepsilon(i\xi) + \sqrt{[\varepsilon(i\xi) - 1] \xi^2 + y^2}} & , \quad r_{\perp}^2(\xi, y) = \left\{ \begin{array}{ll}
\frac{y - \sqrt{[\varepsilon(i\xi) - 1] \xi^2 + y^2}}{y + \sqrt{[\varepsilon(i\xi) - 1] \xi^2 + y^2}}
\end{array} \right. \\
& .
\end{array} \right. \tag{18}$$

By virtue of the fact that $\varepsilon$ depends on temperature through the Matsubara frequencies only, the zero-frequency term of Eq. (16) ($l = 0$) does not contribute into the energy \([3]\) [compare with Eq. (19)]. It is notable also that in the special case of the plasma model the perpendicular reflection coefficient from Eq. (18) is given by

$$r_{\perp}^2(\xi, y) = r_{\perp}^2(y) = \left( \frac{y - \sqrt{\omega_p^2 + y^2}}{y + \sqrt{\omega_p^2 + y^2}} \right)^2, \tag{19}$$

i.e. it is frequency- and temperature-independent for any $l$. By this reason its derivative with respect to temperature does not contribute to energy \([3]\). As a result, in the framework of the plasma model the energy per unit area at a temperature $T$, calculated by Eqs. (3), (16), takes the form

$$E_p^l(a, T) = \frac{k_B T}{8\pi a^2} \sum_{i=1}^{\infty} \xi_i^2 \left[ \ln \Delta_{\parallel}(\xi_i, \xi_i) + \ln \Delta_{\perp}(\xi_i, \xi_i) \right] + \frac{k_B T}{4\pi a^2} \sum_{i=1}^{\infty} \int_{\xi_i}^{\infty} y dy \frac{r_{\parallel}(\xi_i, y)}{e^y - r_{\parallel}^2(\xi_i, y)} \frac{\partial r_{\parallel}(\xi_i, y)}{\partial \xi_i}. \tag{20}$$

This equation is convenient for numerical calculations.

Let us now compare the values of energy at temperature $T$ given by Eq. (20) and free energy of Eq. (14) with the values of energy at zero temperature given by \([3]\) [compare with Eq. (21)].

$$E(a, 0) = \frac{\hbar c}{32\pi^2 a^3} \int_0^{\infty} d\xi \int_{\xi}^{\infty} y dy \left[ \ln \Delta_{\parallel}(\xi, y) + \ln \Delta_{\perp}(\xi, y) \right]. \tag{21}$$

The calculational results at $T = 300$ K for the case of Al with \([1]\)

$$\omega_p = 11.5 \, eV = 1.75 \times 10^{16} \, \text{rad/s} \tag{22}$$

are shown in Fig. 2. In this figure the dimensionless ratios

$$R_p^l = \frac{E_p^l(a, T)}{E_p^l(a, 0)}, \quad \frac{F_p^l(a, T)}{F_p^l(a, 0)} | \frac{E_p^l(a, 0)}{E_p^l(a, 0)} = -1 \tag{23}$$

are plotted by the solid lines 1, 2 and dashed line, respectively, as the functions of the surface separation. The energy at zero temperature $E_p^l(a, 0)$ is computed by Eq. (21) where the plasma dielectric function given by Eq. (14) is substituted. It is clearly seen, that at smallest separations all three quantities (energy at $T = 0$, energy and free energy at $T = 300$ K) have approximately equal values. With an increase of the separation distance the modulus of the relative energy at temperature $T$ decreases to zero limiting value while the modulus of the relative free energy increases. Note that the limiting cases of small and large separations can be simultaneously considered as the limits of low and high temperatures, respectively, if one compares with the so called effective temperature $k_B T_{\text{eff}} = \hbar \omega_p = \hbar c/(2a)$ \([3]\).

The asymptotic behavior of energy and free energy at small and large separations (low and high temperatures) in the case of the plasma model can also be investigated analytically. As was proved in Ref. \([24]\), one can expand Eq. (16) in powers of a small parameter $\lambda_p/2\pi a$, where $\lambda_p$ is the plasma wavelength, and in a contribution, depending on temperature, it would suffice to preserve the first power only. The result valid for all $a \geq \lambda_p$ is

$$F_p^l_E(a, T) = E_p^l(a, 0) - \frac{\hbar c}{8\pi^2 a^3} \sum_{i=1}^{\infty} \left\{ \frac{\pi}{2(2l)^3} \coth(\pi l t) - \frac{1}{(lt)^4} + \frac{\pi^2}{2(2l)^3} \frac{1}{\sinh^2(\pi l t)} \right\} + \frac{\lambda_p}{2\pi a} \left\{ \frac{\pi}{2(2l)^3} \coth(\pi l t) - \frac{4}{(lt)^3} + \frac{\pi^2}{2(2l)^3} \frac{1}{\sinh^2(\pi l t)} + \frac{2\pi^3}{lt} \coth(\pi l t) \right\}, \tag{24}$$
where \( t \equiv T_{\text{eff}}/T \). The quantity \( E^\text{pl}(a,0) \) is the energy at zero temperature. Its expansion in powers of \( \lambda_p/2\pi a \) can be found in Refs. \[12\] (here the result up to fourth order should be used in order to get sufficient accuracy at smallest separations).

From Eq. \( (24) \) the required asymptotics follow. At small separations \( (T \ll T_{\text{eff}}) \) one obtains

\[
F^\text{pl}_E(a,T) = E^\text{pl}(a,0) - \frac{\hbar c \zeta(3)}{16 \pi a^3} \left[ \left( 1 + \frac{\lambda_p}{\pi a} \right) \left( \frac{T}{T_{\text{eff}}} \right)^3 - \frac{\pi^3}{45 \zeta(3)} \left( 1 + 2 \frac{\lambda_p}{\pi a} \right) \left( \frac{T}{T_{\text{eff}}} \right)^4 \right],
\]

(25)

where \( \zeta(z) \) is the Riemann zeta function. Applying the thermodynamical definition \( (3) \) to Eq. \( (25) \), we obtain the low-temperature asymptotic of energy

\[
E^\text{pl}(a,T) = E^\text{pl}(a,0) + \frac{\hbar c \zeta(3)}{8 \pi a^3} \left[ \left( 1 + \frac{\lambda_p}{\pi a} \right) \left( \frac{T}{T_{\text{eff}}} \right)^3 - \frac{\pi^3}{30 \zeta(3)} \left( 1 + 2 \frac{\lambda_p}{\pi a} \right) \left( \frac{T}{T_{\text{eff}}} \right)^4 \right].
\]

(26)

This asymptotic expression is obtained also from Eqs. \( (8) \) or \( (20) \) by the use of the Abel-Plana formula (see Ref. \[28\] where similar calculations were performed).

In the opposite case of large separations \( (T \gg T_{\text{eff}}) \), Eq. \( (24) \) leads to the main contribution of the form

\[
F^\text{pl}_E(a,T) = -\frac{k_B T}{8 \pi a^2} \zeta(3) \left( 1 - \frac{\lambda_p}{\pi a} \right).
\]

(27)

By virtue of Eq. \( (1) \) the asymptotic value of energy is \( E^\text{pl}(a,T) = 0 \). If one wished to have a more exact asymptotic of energy, the next (exponentially small in \( T/T_{\text{eff}} \)) terms omitted in Eq. \( (27) \) should be taken into account or Eq. \( (21) \) should be used. In both cases the result is the same

\[
E^\text{pl}(a,T) = -k_B T^\pi a^2 \left( \frac{T}{T_{\text{eff}}} \right)^2 \left( 1 - 2 \frac{\lambda_p}{\pi a} \frac{T}{T_{\text{eff}}} \right) e^{-2\pi T/T_{\text{eff}}}. \tag{28}
\]

Comparison of the numerical calculations presented in Fig. 2 with calculations by the asymptotic formulas of Eqs. \( (25) \)–\( (28) \) shows that the asymptotic of small separations works well within the separation range \( \lambda_p \leq a \leq 2 - 3 \mu m \), and the asymptotic of large separations is applicable for \( a \geq 5 \mu m \). In the transition range, Eqs. \( (14), (20) \) should be used to calculate the values of the free energy and energy for the thermal Casimir force in the framework of the plasma model.

If we consider the limit \( \omega_p \to \infty \) (\( \lambda_p \to 0 \)) in Eqs. \( (24) \)–\( (28) \), the results for ideal metal are obtained.

### IV. DIFFERENT APPROACHES TO THE CALCULATION OF ENERGY AND FREE ENERGY IN THE FRAMEWORK OF THE DRUDE MODEL

Let us now consider metals described by the Drude dielectric function

\[
\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} , \quad \varepsilon(i\xi) = 1 + \frac{\omega_p^2}{\xi(\xi + \tilde{\gamma})},
\]

(29)

where \( \gamma \) is the relaxation parameter. In terms of a dimensionless frequency introduced in Eq. \( (14) \), the Drude dielectric function along the imaginary axis is

\[
\tilde{\varepsilon}(i\tilde{\xi}) = 1 + \frac{\tilde{\omega}_p^2}{\tilde{\xi}(\tilde{\xi} + \tilde{\gamma})} , \quad \tilde{\gamma} \equiv \frac{2a}{c} \gamma.
\]

(30)

As was noticed in the introduction, there is no agreement in the recent literature regarding the use of the Drude model in the framework of the Lifshitz theory. Because of this, it is appropriate to reexamine the applicability of the Drude model in the context of the thermal Casimir force. The Drude model, as opposed to the plasma model, takes into account the phenomenon of volume relaxation. In reality, this phenomenon plays a role in the domain of the normal skin effect where the mean free path \( l \) of the electron is much less than the penetration depth of the electromagnetic oscillations into a metal \( \delta \) and the mean distance \( \nu/\omega \) traveled by an electron in a time \( 1/2\pi \) of the period of the electromagnetic field \[12,14\]. For most of metals at \( T = 300 \) K the domain of the normal skin effect
extends from the quasistatic fields (where $\varepsilon$ is pure imaginary) to the frequencies of order $10^{12}$ rad/s. What this means is that the Drude dielectric function has a direct relationship only to plate separations $0.1 \text{ cm} < a < 1 \text{ km}$ such that the characteristic frequency $\omega_c = e^2/(2a)$ belongs to this domain. However, at so large separations the Casimir force is extremely small and is of academic interest only.

For higher frequencies, depending on which metal is considered, the anomalous skin effect ($\delta \ll l$, $\delta \ll v/\omega$) or relaxation region ($v/\omega \ll l \ll \delta$) occur. Here the volume relaxation described by the parameter $\gamma$ is not significant, but, in general, the space dispersion gives an important contribution. Note that in the domain of the anomalous skin effect (it extends up to around $7 \times 10^{13}$ rad/s) metal cannot be described by either the Drude model, given by Eqs. (29), (30), or by any dielectric function depending only on frequency as well.

On further increase of frequency, the transition to the infrared optics occur, where $v/\omega \ll \delta \ll l$ (or to the “extremely anomalous skin effect” if we use Casimir’s terminology [14]). In this domain the volume relaxation does not play any role. In the semiclassical theory of AC conductivity $\varepsilon$ is practically real, signifying no dissipation of the electromagnetic energy within the metal [45]. Because of this, the plasma model is realistic if the characteristic frequency $\omega_c$ belongs to the domain of the infrared optics (see Sec. III). This domain extends to the frequencies of around $2 \times 10^{18}$ rad/s and for higher frequencies is followed by the domain of the ultraviolet transparency of metals. However, some interelectronic collisions and a scattering on the surface lead to a small imaginary part of $\varepsilon$ in the domain of infrared optics [46] as is demonstrated by the optical tabulated data for complex refraction index [41]. These data are often used to find the values of $\varepsilon(\xi)$ along the imaginary axis through the dispersion relation [22,23,24,25]. By way of example, for Al the optical data for $\omega \geq 6.08 \times 10^{13}$ rad/s are tabulated [41].

At the same time, the existence of the anomalous skin effect domain, where the concept of $\varepsilon(\omega)$ is not applicable, is usually ignored, and the optical tabulated data are theoretically extended into the domain of lower frequencies by means of the Drude dielectric function [41]. This is needed to compute the dispersion integral from zero to infinity. The values of $\varepsilon(\xi)$ obtained in such a manner by means of the dispersion relation and extended tabulated data are satisfactory up to $\xi \sim 10^{15}$ rad/s with $\varepsilon(\xi)$ obtained by the immediate substitution of the imaginary frequency into the Drude model according to Eq. (29) with no use of the dispersion relation. This suggests that the Drude model can be applied for the calculation of the Casimir force within a micrometer domain $a \geq 0.4 \mu m$ in parallel with the plasma model. It should be particularly emphasized, however, that the application of the Drude model in the domain of infrared optics is physically unjustified as the volume relaxation is absent in this domain (below we call into question also the possibility to substitute the Drude dielectric function into the zero-frequency term of the Lifshitz formula).

In contrast to the case considered in Sec. II, the Drude metals are dissipative media, described by the complex $\varepsilon(\omega)$. At a given frequency $\varepsilon$ depends explicitly on temperature through the relaxation parameter $\gamma$. Because of this, the energy of the equilibrium fluctuating electromagnetic field cannot be presented any more in the simple form of Eq. (7). In accordance with the thermodynamic equality (8), additional terms appear in the right-hand side of Eq. (7) containing the derivatives $\partial \omega^{(\parallel, \perp)} / \partial T$ [33].

Substituting Drude dielectric function [32] into the Lifshitz formula for the free energy [16] and using the definition [1] of energy at temperature $T$, one obtains

$$E^D(a, T) = -\frac{k_B T^2}{16\pi^2 a^2} \frac{\partial f_0^{(a,b,c)}(a, T)}{\partial T} + \frac{k_B T}{8\pi^2 a^2} \sum_{l=1}^{\infty} \xi_l^2 \left[ \ln \Delta_{\parallel}(\tilde{\xi}_l, \tilde{\xi}_l) + \ln \Delta_{\perp}(\tilde{\xi}_l, \tilde{\xi}_l) \right]$$

$$+ \frac{k_B T}{4\pi^2 a^2} \sum_{l=1}^{\infty} \int_{\tilde{\xi}_l}^{\infty} y dy \left[ \frac{r_{\parallel}(\tilde{\xi}_l, y)}{e^y - r_{\parallel}^2(\tilde{\xi}_l, y)} \left( T \frac{\partial r_{\parallel}(\tilde{\xi}_l, y)}{\partial \gamma} \frac{\partial \gamma}{\partial T} + \gamma \frac{\partial r_{\parallel}(\tilde{\xi}_l, y)}{\partial T} \frac{\partial \gamma}{\partial T} \right) \right]$$

$$+ \frac{r_{\perp}(\tilde{\xi}_l, y)}{e^y - r_{\perp}^2(\tilde{\xi}_l, y)} \left[ T \frac{\partial r_{\perp}(\tilde{\xi}_l, y)}{\partial \gamma} \frac{\partial \gamma}{\partial T} + \gamma \frac{\partial r_{\perp}(\tilde{\xi}_l, y)}{\partial T} \frac{\partial \gamma}{\partial T} \right] \right\}.$$  

Here the zero-frequency term of Eq. (16) is separated because there is disagreement in recent literature on whether or not it contributes to the Casimir energy and force. The immediate consequence of Eqs. (7), (16), (30) [approach a) described in Introduction] is [22]

$$f_0^{(a)}(a, T) = \int_0^\infty dy y \ln \left( 1 - e^{-y} \right) = -\zeta(3).$$

This result is given by the parallel modes only, while the perpendicular modes do not contribute.

The special modification of the zero-frequency term of Eq. (16) proposed in [22] [approach b)] leads to

$$f_0^{(b)}(a, T) = -\zeta(3) + \int_0^\infty dy y \ln \left[ 1 - r_{\perp}^2(y, y) e^{-y} \right].$$
The two contributions in the right-hand side of Eq. (33) are given by the parallel (perpendicular) modes, respectively. If for real metals the same prescription is used as for ideal metal [approach c]), one obtains

\[ f_0^{(c)}(a, T) = 2 \int_0^\infty dy y \ln (1 - e^{-y}) = -2\zeta(3), \quad (34) \]

where both polarizations lead to equal nonzero contribution. Evidently, in the framework of the approaches a) and c) the zero-frequency term is temperature independent and does not contribute to the energy (31). In the framework of the approach b) there is only a fair contribution due to the dependence of \( r_\perp(y, y) \) on \( \gamma(T) \) in Eq. (33).

Note that Eq. (31) is in direct analogy to Eq. (20). The additional terms which are present in Eq. (31) take into account the explicit dependence of the dielectric permittivity on temperature through the relaxation parameter. This equation is convenient for the numerical calculations.

Before performing the calculations, let us give the approximate expressions for both free energy and energy which allow one to compare the results obtained in the framework of the Drude and plasma models. For this purpose we expand Eq. (16) in powers of a small parameter \( \alpha = \lambda_\rho/4\pi a = 1/\omega_p \). The result is

\[ F^D_F(a, T) = F^{pl}_F(a, T) + \frac{k_B T}{16\pi a^2} \left( f_0^{(a,b,c)}(a, T) + \zeta(3) - \int_0^\infty dy y \ln (1 - r_\perp^2(y)e^{-y}) \right) + \frac{\gamma}{\omega_p} \frac{k_B T}{4\pi a^2} \sum_{l=1}^\infty \left[ \oint_{\xi_l} dy \frac{dy}{e^y - 1} + \frac{1}{\xi_l} \oint_{\xi_l} dy \frac{y^2}{e^y - 1} \right], \quad (35) \]

where \( F^D_F(a, T) \) is the free energy in the plasma model given by Eq. (24), and \( r_\perp(y, y) \) is defined in Eq. (13). It is notable that the results of numerical calculations by this formula and by Eqs. (16), (31) (with different approaches to the zero-frequency term) coincide with an accuracy of 0.06% at \( a = 0.4 \mu m \) and better than 0.01% for \( a \geq 3 \mu m \). Note, as discussed above, the Drude model leads to satisfactory \( \epsilon(T, a, T) \) in the framework of the Drude and plasma models, dependent on the approach used:

\[ \Delta F^0_E = F^D_F - F^{pl}_F, \]

computed in the framework of the Drude and plasma models, depends on the approach used:

\[ \Delta F^0_{E(a)} = -\frac{k_B T}{16\pi a^2} \int_0^\infty dy y \ln (1 - r_\perp^2(y)e^{-y}), \quad (36) \]

\[ \Delta F^0_{E(b)} = \frac{k_B T \gamma(T)}{8\pi a^2 \omega_p} \oint_0^\infty dy \frac{dy}{e^y - 1} = \frac{\pi k_B T \gamma(T)}{48\pi a^2} \omega_p, \quad (37) \]

\[ \Delta F^0_{E(c)} = -\frac{k_B T}{16\pi a^2} \left\{ \zeta(3) - \int_0^\infty dy y \ln (1 - r_\perp^2(y)e^{-y}) \right\}, \quad (38) \]

In the case of approaches a) and c), the difference of the free energies contains linearly decreasing with temperature terms [Eqs. (29), (31)]. In the case of approach b), owing to the relaxation parameter, \( \Delta F^0_E \) falls off more quickly with decreasing temperature [the same is true for \( F^{pl}_F \), as is seen from Eq. (25), and for the summation term in the right-hand side of Eq. (31)]. It should be particularly emphasized that the presence of the linear terms in temperature in the free energy is in contradiction with the requirements of thermodynamics (see Sec. V).

To obtain the approximate perturbative expression for the energy by analogy with Eq. (33), one should use the explicit dependence of \( \gamma \) on temperature. It has been known that at temperature \( T > T_D/4 \), where \( T_D \) is the Debye temperature (for \( Al T_D = 428 K \) [17]), \( \partial\gamma/\partial T = \gamma(T) \), i.e. \( \gamma \) is linear in temperature. Generally, \( \partial\gamma/\partial T = \nu \gamma(T) \) with \( \nu = \nu(T) \geq 1 \). In Fig. 3, the dependence of \( \gamma \) on temperature is plotted for \( Al \) on the basis of tabulated data [7]. Finally, the required expression is

\[ E^D(a, T) = E^{pl}(a, T) + \epsilon_0^{(a,b,c)}(a, T) + \frac{k_B T}{16\pi a^2 \omega_p} \gamma \sum_{l=1}^\infty \left[ \frac{2\xi_l^2}{e^{\xi_l} - 1} - (\nu + 1)\xi_l \oint_{\xi_l} dy \frac{dy}{e^y - 1} - \frac{\nu - 1}{\xi_l} \oint_{\xi_l} dy \frac{y^2}{e^y - 1} \right], \quad (39) \]

where \( \epsilon_0^{(a)} = \epsilon_0^{(c)} = 0 \), and
\[ e_0^{(b)}(a, T) = -\frac{\pi k_B T}{4a^2} \nu \gamma. \]

In Fig. 4 the results of the numerical calculations are shown for Al described by the Drude model in different approaches at \( T = 300 \text{K} \). In the vertical axis the dimensionless ratios are plotted

\[ \frac{R^D}{|E^D(a, 0)|} = -1 \]

as a function of the surface separation. Curve 1 shows the behavior of the relative energy (which is practically the same in all three approaches); curves 2a, 2b and 2c show the relative free energy in the approaches a), b), and c), respectively. The dashed curve is for the energy at zero temperature. All calculations are performed both using the exact expressions (16), (17) and the approximate ones (33), (34) with coinciding results.

It is important to explain in more detail the notation \( E^D(a, 0) \). It is the value of energy in the framework of the Drude model (33), computed at zero temperature in the sense that Eq. (2) with a double integral instead of a discrete sum is employed. At the same time, in calculations of \( E^D(a, 0) \) the value of the relaxation parameter \( \gamma \) at \( T = 300 \text{K} \) is used. We divide the calculational results into this hybrid quantity, previously used in literature (see, e.g., Refs. 22, 23, 24, 25). This allows one to associate this quantity with energy and free energy in order to clarify its physical meaning.

As is seen from Fig. 4, curve 1, illustrating the equal behavior of energy in all three approaches, and curve 2b, illustrating the behavior of free energy as given by the approach b), demonstrate plausible properties. Among other things, the free energy approaches energy with a decrease of the surface separation distance (compare with Fig. 2 in the case of the plasma model). As to the curves 2a and 2c, representing the free energy in the approaches a) and c), they do not approach to each other nor to energy within the application range of the Drude dielectric function. Note that even at separations of about 0.4 – 0.5 \( \mu \text{m} \) the free energy \( F_E \) (curve 2a), obtained by the direct application of the Lifshitz formula, differs by 8\% from the double integral \( E^D(a, 0) \) (dashed line).

An important point is that not only the free energy of curve 2a but also 2b and 2c, and energy of curve 1 do not approach the dashed line in Fig. 4 representing the quantity which is in common use as a measure of energy at zero temperature \( 1, 2, 23, 24, 27 \). This is clearly seen from Fig. 5 where the curves 1, 2b and 2c are reproduced on an enlarged scale for the smallest separations where the Drude model is applicable. The long-dashed curve 3 in Fig. 5 illustrates the dependence of one more quantity on surface separation defined as

\[ R^D = \frac{E^D_\gamma(a, T)}{|E^D(a, 0)|} \]

where \( E^D_\gamma \) is the energy at a temperature \( T \) computed on the assumption that \( \gamma \) does not depend on temperature (and preserves its value as at \( T = 300 \text{K} \)). Curve 3 is computed by Eq. (31) with \( \partial \gamma / \partial T = 0 \). The same curve is obtained by the application of the approximate Eq. (39) with \( \nu = 0 \).

From Fig. 5 we notice that curve 3 approaches the short-dashed curve with a decrease of a separation distance. Because of this, it may be concluded that the hybrid quantity \( E^D(a, 0) \) computed in the literature is in fact some approximation for \( E^D_\gamma \), i.e. for the energy at temperature \( T \) computed without regard for the explicit dependence of the dielectric properties on temperature [remind that this kind dependence is absent in the case of the plasma model (see Secs. II, III) but is essential for metals described by the Drude model]. From Fig. 5 it follows that at a separation of 0.5 \( \mu \text{m} \) \( E^D(a, 0) \) departs from the correct value of energy (curve 1) by approximately 0.75\%. As to the free energies of the approaches a) and c), the deviations are larger (8\% and 3.3\%, respectively; these approaches are in contradiction with thermodynamics, see Sec. V). The above deviations should be added to the errors of \( E^D(a, 0) \), discussed in Ref. 23, that are connected with uncertainties in the optical tabulated data.

V. ENTROPY FOR THE THERMAL CASIMIR FORCE BETWEEN REAL METALS

Considerations of the entropy of the fluctuating field in dependence on temperature allows one to test different approaches discussed above for conformity to thermodynamics. Entropy of the fluctuating electromagnetic field can be expressed in terms of a free energy

\[ S(a, T) = -\frac{\partial F_E(a, T)}{\partial T} \]

where
or, taking into account Eq. (1), identically, as

$$ S(a, T) = -\frac{1}{T} [E(a, T) - F_E(a, T)]. \tag{44} $$

So it can be simply computed by the use of the results for the free energy and energy obtained in Secs. III, IV.

Let us start with the plasma model where the analytical calculation is possible [approach d)]. At small separations (low temperatures) one can use Eqs. (25), (26) for the free energy and energy, respectively ($a \geq \lambda_p$ is supposed). Then both Eqs. (43) and (44) lead to the same result

$$ S^{pl}(a, T) = \frac{3k_B \zeta(3)}{8\pi a^2} \left( \frac{T}{T_{eff}} \right)^2 \left[ 1 - \frac{4\pi^3}{135\zeta(3)} \frac{T}{T_{eff}} + \frac{\lambda_p}{\pi a} \left[ 1 - \frac{8\pi^3}{135\zeta(3)} \frac{T}{T_{eff}} \right] \right]. \tag{45} $$

Note that this expression was first obtained in Ref. [34] with errors in numerical coefficients, because in Ref. [34] the energy of thermal photons was not taken properly into account. At large separations (high temperatures) the asymptotic expressions (27), (28) are applicable leading to

$$ S^{pl}(a, T) = \frac{k_B \zeta(3)}{8\pi a^2} \left( 1 - \frac{\lambda_p}{\pi a} \right) \tag{46} $$

(we have omitted exponentially small terms in $2\pi T/T_{eff}$). In the limit of $\lambda_p \to 0$ Eqs. (45), (46) lead to the values of entropy for plates made of ideal metal

$$ S(a, T) = \frac{3k_B \zeta(3)}{8\pi a^2} \left( \frac{T}{T_{eff}} \right)^2 \left[ 1 - \frac{4\pi^3}{135\zeta(3)} \frac{T}{T_{eff}} \right], \quad S(a, T) = \frac{k_B \zeta(3)}{8\pi a^2} \tag{47} $$

for $T \ll T_{eff}$, $T \gg T_{eff}$, respectively. The results (47) coincide with those obtained for an ideal metal in Ref. [49]. Asymptotic behavior of the entropy for an ideal metal in a high temperature limit was obtained also in Ref. [49]. The result of (47) is, however, two times smaller than in Eq. (17) and Ref. [48] due to an error contained not only in the entropy but also in the expression for the Casimir energy between two plates made of ideal metal at zero temperature as is used in Ref. [49].

It is obvious that Eq. (45) leads to nonnegative values of entropy with $S^{pl}(a, 0) = 0$ as is demanded by the third law of thermodynamics (the Nernst heat theorem [50]).

We now direct our attention to the entropy in the framework of the Drude model. As before, numerical calculations can be performed by the exact formulas for the energy and free energy or by the approximate ones valid at $a \geq \lambda_p$ with coinciding results. From Eqs. (33), (43) one obtains

$$ S^D(a, T) = S^{pl}(a, T) + S^{(a,b,c)}_0(a, T) + \frac{k_B}{4\pi a^2} \sum_{l=1}^{\infty} \left[ \frac{2\xi^2}{e^{\xi^2} - 1} - (\nu + 2)\xi \int_{\xi_l}^{\infty} \frac{dy}{e^y - 1} - \nu \int_{\xi_l}^{\infty} \frac{dy}{e^y - 1} \right]. \tag{48} $$

Here $S^{pl}(a, T)$ is the entropy in the framework of the plasma model computed by Eqs. (24), (33), and $S^{(a,b,c)}_0(a, T)$, defined by

$$ S^{(a,b,c)}_0(a, T) = -\frac{k_B}{16\pi a^2} \frac{\partial}{\partial T} \left\{ T \left[ f_0^{(a,b,c)}(a, T) + \zeta(3) - \int_0^{\infty} dy y \ln \left( 1 - r^2_y(y)e^{-y} \right) \right] \right\}, \tag{49} $$

describes the contribution of the zero-frequency term of the Lifshitz formula into entropy in different approaches. Using the same perturbation expansions as in Sec. IV, one obtains

$$ S^{(a)}_0(a, T) = -\frac{k_B \zeta(3)}{16\pi a^2} \left[ 1 - 2 \frac{\lambda_p}{\pi a} + 3 \frac{\lambda_p^2}{\pi^2 a^2} \right], $$

$$ S^{(b)}_0(a, T) = -\frac{k_B \pi}{48a^2} (\nu + 1) \frac{\gamma}{\omega_p}, \tag{50} $$

$$ S^{(c)}_0(a, T) = \frac{k_B \zeta(3) \lambda_p}{8\pi a^2} \left( 1 - \frac{3 \lambda_p}{2 \pi a} \right). $$

The results of numerical calculations using Eqs. (45), (47) for $a = 2 \mu m$ are presented in Fig. 6. As is seen from the figure, in the approach a) entropy is negative in a wide temperature range from $T = 0$ to almost $T = 300 K$, which is
a nonphysical result. In the approach a) entropy preserves the negative sign for lesser separations between the plates as well. In the approaches b), c) entropy is positive as it must be. In the approach b) \( S^D(a, 0) = 0 \), whereas in the approaches a), c) \( S^D(a, 0) \neq 0 \) which is in contradiction with the Nernst heat theorem. From Eqs. (48), (50) it follows that

\[
S^D(a, 0) = S_0^{a,b,c}(a, 0),
\]

\[
S_0^{(b)}(a, 0) = 0, \quad S_0^{(c)}(a, 0) - S_0^{(a)}(a, 0) = \frac{k_B \zeta(3)}{16\pi a^2},
\]

where the absolute values of \( S_0^{a,c}(a, 0) \) are given by Eq. (50). They are not only different from zero but depend on the parameters of the system (plate separation distance and plasma wavelength) which is prohibited by the third law of thermodynamics [48]. Because of this, approaches a) and c) must be rejected. Note also that approach a) predicts nonzero value of entropy at zero temperature for an ideal metal in contradiction with the field-theoretical result of Ref. [48]. As for approaches b) and d), based on the special modification of the zero-frequency term of the Lifshitz formula and on the use of the plasma model, respectively, they are in agreement with the requirements of thermodynamics. To decide between them some additional considerations, which are presented in the next section, are needed.

VI. CONCLUSIONS AND DISCUSSION

In the above the correlation between the Casimir energy and the free energy at a temperature \( T \) is investigated for the case of two plane parallel plates made of real metal. It is shown that for the nondissipative media described by the real dielectric permittivity with no explicit dependence on temperature the photons between plates can be considered as the elementary excitations of the electromagnetic field interacting with a matter of plates. In this case the energy at temperature \( T \) is proved to be a sum of the (renormalized) energy of zero-point oscillations and thermal photons. If the media are dissipative and their dielectric permittivity depends on temperature, the simple picture above is not correct. The concept of thermal photons loses immediate significance and the energy of fluctuating field contains additional terms depending on the derivatives of the dielectric permittivity with respect to temperature.

The expression for the energy at a temperature \( T \) found in this paper helps to elucidate the meaning of the so called “Casimir energy at zero temperature” calculated by many authors as a double integral using the Drude model and optical tabulated data at room temperature (note that this quantity is of great importance as it is proportional to the Casimir force in the configuration of a sphere or a spherical lens above a plate used in experiments [24,30,31,35]). The commonly accepted opinion that the above-mentioned quantity is approximately equal to the free energy at small temperatures (small separations) is inexact. In fact, even at rather small separations the “Casimir energy at zero temperature” deviates from the free energy by several percent but approaches to the energy at room temperature calculated on the assumption that the dielectric permittivity does not depend on \( T \) explicitly (this assumption is not correct in the case of the Drude dielectric function).

Different approaches to describe the thermal Casimir force from recent literature were compared and analysed [approaches a), b), c) in the framework of the Drude model and approach d) in the framework of the plasma model - see Introduction]. The quantitative expressions for the entropy of the fluctuating field are obtained here for the first time in the case of real metals. They give the possibility to conclude that the approaches a) and c) are in contradiction with the principles of thermodynamics and must be rejected. The approaches b) and d) are found to be in agreement with thermodynamics.

To make a choice between the approaches b) and d) let us discuss the behavior of the dielectric permittivities of the plasma and Drude models at small frequencies. Several authors [24,30,31,35] give preference to the Drude model because it shows \( \omega^{-1} \) frequency dependence of the dielectric permittivity at small frequencies as it follows from Maxwell equations (compare with \( \omega^{-2} \) frequency dependence given by the plasma model). Although this statement is true, it should be remembered that the Drude model is not applicable at all frequencies. We note that the concept of \( \varepsilon(\omega) \) itself, not only the Drude model, does not work in the domain of the anomalous skin effect (see Sec. IV). As to the quasistatic limit, although \( \varepsilon(\omega) \) is of order \( \omega^{-1} \) in this domain, the Drude model is also not applicable as the correct \( \varepsilon(\omega) \) is pure imaginary. Since the zero-frequency term of the Lifshitz formula necessarily belongs to the domain of the quasistatic fields, where the concept of traveling waves fails, the substitution of the Drude dielectric function into this term (resulting in all the above problems) seems to be unjustified.

To clarify the situation with the thermal Casimir force, let us consider two pairs of plane parallel plates \( \varepsilon = 5 \mu \text{m} \) apart made of Al (one pair of plates) and of indium tin oxide (the other one). Due to large separation distance, the
asymptotic of high temperatures is applicable and only the zero-frequency term of the Lifshitz formula determines the total value of the Casimir force. At quasistatic frequencies both Al and indium tin oxide are good conductors. Because of this, the Lifshitz formula would lead to one and the same Casimir force at 5 \( \mu \)m separation for both pairs of plates if one substitutes into it the actual reflection properties of these materials at zero frequency. This conclusion is in contradiction with intuition. Note that an indium tin oxide is transparent to visible and near infrared light. Within a wide wavelength range 7 \( \mu \)m < \( \lambda < 100 \) \( \mu \)m around the characteristic wavelength \( \lambda_c = 62.8 \) \( \mu \)m (the latter corresponds to the characteristic frequency \( \omega_c = c/2a = 3 \times 10^{14} \) rad/s), giving the main contribution into the Casimir force at zero temperature. \( \omega > \lambda \), the reflectivity of indium tin oxide is below 80% \( \alpha \). Note that the second parameter of the problem, first Matsubara frequency, is \( \omega_M = 2\pi k_B T/\hbar = 2.45 \times 10^{14} \) rad/s, i.e. \( \lambda_M = 7.7 \) \( \mu \)m, which belongs to the region of even larger transparency of indium tin oxide. In this situation it is difficult to imagine that at \( a = 5 \) \( \mu \)m the indium tin oxide plates are attracted with the same Casimir force as Al plates which are almost perfect reflectors within a wide range around the characteristic wavelength.

We can avoid this contradiction between the literally understood theory and physical intuition if we assume that it is not correct to substitute the actual behavior of the dielectric permittivity at zero frequency into the Lifshitz formula. Instead, in order to obtain the physically correct results, the frequency dependence of the dielectric permittivity and reflection coefficients around the characteristic frequency should be extrapolated to zero Matsubara frequency and substituted into the Lifshitz formula. If this conjecture is accepted, one should conclude that within the range of micrometer separation distances between plates the plasma model dielectric function, i.e. the approach d), is preferable as compared with the use of the Drude dielectric function combined with any of the above approaches a), b), c). It is apparent from the fact that the plasma dielectric function and respective reflection coefficients admit reasonable continuation from the range of infrared optics to zero frequency.

The contradictions discussed in this paper lead to a conclusion that the concepts of the frequency dependent dielectric permittivity and fluctuating electromagnetic field inside media in application to the thermal Casimir force between real metals are inadequate idealizations. Less sophisticated approaches, such as the surface impedance approach (the Leontovich boundary conditions), which does not consider the fluctuating field inside matter, appear to be more adequate and lead to physically justified results for all separation distances between plates. By way of example, in the domain of the infrared optics the surface impedance leads to the same results as the Lifshitz formula in combination with the plasma model [approach d)]. If the characteristic frequency belongs to the domain of the normal skin effect, where the Drude model is physically correct, there is no reasonable continuation of \( \varepsilon \) to zero frequency avoiding the above problems. At the same time, the impedance approach, when applied in the domain of the normal skin effect, leads to quite satisfactory results coinciding with those for ideal metal as it must be at separations larger than 0.1 cm [almost the same results are given in this domain by the approaches b), c)].

To conclude, at present the impedance approach can be considered as the most universal, reliable and straightforward way to calculate the thermal Casimir force between real metals at different separation distances. In the domain of micrometer separations the plasma model is also realistic. Regarding the Drude model, it can be used to describe the thermal Casimir force only with some appropriate modification of the zero-frequency term of the Lifshitz formula [like in the approach b), for instance].

ACKNOWLEDGMENTS

G.L.K. is greatly indebted to I. E. Dzyaloshinskii for helpful discussions. The authors are grateful to U. Mohideen for valuable remarks. They acknowledge the financial support from CNPq.

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FIG. 1. Integration path $C$ in the plane of complex frequency. The Matsubara frequencies are $\xi_l$ and photon eigenfrequencies are $\omega_n$. 
FIG. 2. Relative energy at temperature $T = 300\,\text{K}$ (curve 1), free energy (curve 2), and energy at zero temperature (dashed line) versus surface separation in the framework of the plasma model.
FIG. 3. Relaxation parameter of $Al$ versus temperature.
FIG. 4. Relative energy at temperature $T = 300$ K (curve 1), free energy [curve 2a in the approach a), curve 2b in the approach b), and curve 2c in the approach c)], and energy at zero temperature (dashed line) versus surface separation in the framework of the Drude model.
FIG. 5. Relative energy at temperature $T = 300\,\text{K}$ (curve 1), free energy [curve 2b in the approach b) and curve 2c in the approach c)], and energy at zero temperature (short-dashed line) versus surface separation in the framework of the Drude model reproduced on an enlarged scale. Long-dashed curve 3 presents energy computed on the assumption that dielectric permittivity does not depend on temperature.
FIG. 6. Entropy of fluctuating electromagnetic field in the framework of the Drude model versus temperature computed on the basis of approaches a), b), and c) (curves a, b and c, respectively).