

Low-temperature behavior of the Casimir free energy and entropy of metallic filmsG. L. Klimchitskaya^{1,2} and V. M. Mostepanenko^{1,2,3}¹*Central Astronomical Observatory at Pulkovo of the Russian Academy of Sciences, Saint Petersburg 196140, Russia*²*Institute of Physics, Nanotechnology and Telecommunications, Peter the Great Saint Petersburg Polytechnic University, Saint Petersburg 195251, Russia*³*Kazan Federal University, Kazan 420008, Russia*

(Received 21 November 2016; published 24 January 2017)

We derive an analytic behavior of the Casimir free energy, entropy, and pressure of metallic films in a vacuum at low temperature. It is shown that this behavior differs significantly depending on whether the plasma or the Drude model is used to describe the dielectric properties of film metal. For metallic films described by the lossless plasma model the thermal corrections to the Casimir energy and pressure drop to zero exponentially fast with increasing film thickness. There is no classical limit in this case. The Casimir entropy satisfies the Nernst heat theorem. For metallic films with perfect crystal lattices described by the Drude model, the Casimir entropy at zero temperature takes a nonzero value depending on the parameters of a film, i.e., the Nernst heat theorem is violated. The Casimir entropy at zero temperature is positive, as opposed to the case of two metallic plates separated with a vacuum gap, where it is negative if the Drude model is used. Possible applications of the obtained results in investigations of the stability of thin films are discussed.

DOI: [10.1103/PhysRevA.95.012130](https://doi.org/10.1103/PhysRevA.95.012130)**I. INTRODUCTION**

During the last few years the van der Waals and Casimir interactions have attracted widespread interest due to important role they play in many physical phenomena [1,2]. In most cases, however, the emphasis has been made on the forces acting between two closely spaced bodies, be it two atoms or molecules, an atom or a molecule and a macroscopic surface, or two macroscopic surfaces. It is common knowledge that the van der Waals and Casimir forces are caused by the zero-point and thermal fluctuations of the electromagnetic field and are described by the Lifshitz theory of dispersion forces [3]. At the moment these forces are being actively investigated not only theoretically but also experimentally (see Refs. [4,5] for a review) and are used in technological applications [6–8].

Another important role of dispersion interactions is that they contribute to the free energy of free-standing material films and films deposited on some material plates. The formulation of this problem goes back to Derjaguin, who took into account the dispersion-force contribution in studies of stability of thin films and introduced the concept of disjoining pressure (see Refs. [9,10] for a review). Over a few decades this contribution to the free energy, which depends on the film thickness, was estimated using the power-type force law and the Hamaker constant.

In the present state of the art, the question of the Casimir energy for a free-standing or sandwiched between two dielectric plates metallic film was raised in Ref. [11]. Then the Casimir energy of a free-standing in vacuum metallic film was considered in Refs. [12,13]. In doing so, the dielectric properties of metal were described by either the Drude or the plasma model. When employing the plasma model, the Lifshitz theory at nonzero temperature has been used in calculations. However, all calculations employing the Drude model have been performed at zero temperature. This did not allow revelation of significant differences in theoretical results for the free energy of metallic films predicted by the Lifshitz theory combined with either the Drude or the plasma model.

Full investigation of the Casimir free energy and pressure for metallic films in the framework of the Lifshitz theory at nonzero temperature was performed in Refs. [14–16]. The cases of free-standing or sandwiched between two dielectric plates [14] deposited on a metal plate [15] or made of magnetic metal [16] metallic films have been considered. The dielectric properties of metals were described by using the optical data for the complex index of refraction extrapolated to zero frequency by the Drude or plasma models. It was shown that magnitudes of the free energy of metallic films of less than 150 nm thickness differ by up to a factor of 1000 depending on the calculation approach used [14–16]. So great difference is explained by the fact that the Casimir free energy of metallic films drops to zero exponentially fast when the plasma model is used for extrapolation and goes to the classical limit when the optical data are extrapolated by the Drude model [14–16]. This limit is already reached for the film of 150 nm thickness.

Here we note that although routinely it is quite natural to use the Drude model for extrapolation of the optical data to lower frequencies because it takes into account the relaxation properties of conduction electrons, there are also strong reasons for using the lossless plasma model for this purpose in the case of fluctuating fields. The point is that the measurement data of all precise experiments on measuring the Casimir interaction between two material bodies separated with a vacuum gap exclude theoretical predictions of the Lifshitz theory combined with the Drude model and are consistent with predictions of the same theory using the plasma model [17–23]. For the gap width below $1\ \mu\text{m}$, used in these experiments, the variation in theoretical predictions of both approaches is below a few percent. Recently, however, the differential force measurement scheme has been proposed [24–26], where this variation is by up to a factor 1000. The results of one of these experiments, already performed [27,28], exclude with certainty the predictions of the Drude model and are consistent with the plasma model. Based on this, it was hypothesized that the reaction of a physical system to

real and fluctuating electromagnetic fields (having a nonzero and zero expectation values, respectively) might be different [16,29].

On the theoretical side, it was shown [30,31] that for two metallic plates, separated by more than $6\ \mu\text{m}$ distance, the classical statistical physics predicts the same Casimir force as does the Lifshitz theory combined with the plasma model. By contrast, for metals with perfect crystal lattices the Lifshitz theory was shown to violate the third law of thermodynamics (the Nernst heat theorem) when the Drude model is used [32–36]. In this respect, one may guess that even at separations exceeding $6\ \mu\text{m}$, where the major contribution to the Casimir force between two parallel plates becomes classical, the quantum effects still remain important and make the classical treatment inapplicable.

In view of the above problem, which is often called “the Casimir puzzle,” it is desirable to present additional arguments regarding an applicability of the Drude and plasma models in calculations of the Casimir free energy of metallic films. Here the calculation results differ greatly, and the subject is not of only an academic character because the obtained values should be taken into account in the conditions of film stability.

In this paper, we derive the asymptotic expressions at low temperature for thermal corrections to the Casimir free energy and pressure of metallic films described by the plasma model. The asymptotic behavior of the Casimir entropy is also obtained. Unlike the familiar case of two parallel plates separated with a gap, all these quantities decrease exponentially fast with increasing film thickness and do not have the classical limit by depending on \hbar at arbitrarily large film thicknesses. It is shown that the Casimir entropy of a film preserves the positive values and, in the limiting case of zero temperature, goes to zero. Thus, it is proved that the Casimir entropy of metallic films described by the plasma model satisfies the Nernst heat theorem, i.e., the Lifshitz theory is thermodynamically consistent.

Then the low-temperature behavior of the Casimir free energy and entropy for metallic films described by the Drude model is considered. We show that in the limiting case of zero temperature the Casimir entropy goes to a positive value depending on the parameters of a film. Therefore, the Nernst heat theorem is violated [37,38]. Furthermore, it is demonstrated that in this case the Casimir free energy does not go to zero in the limiting case of ideal metal film, which is in contradiction to the fact that electromagnetic oscillations cannot penetrate in an interior of ideal metal. Thus, the description of a film metal by the Drude model in the Lifshitz theory results in violation of basic thermodynamic demands. Because of this, the dispersion-force contribution to the free energy of metallic films might need a reconsideration taking into account that the low-frequency behavior of the film metal is described by the plasma model.

The paper is organized as follows. In Sec. II we present a general formalism and derive the low-temperature behavior of the Casimir free energy, pressure, and entropy for metallic films described by the plasma model. In Sec. III we consider the low-temperature behavior of the Casimir free energy and entropy of metallic films with perfect crystal lattices described by the Drude model and demonstrate violation of the Nernst heat theorem. Section IV contains our conclusions and

discussion. In the Appendix, some details of the mathematical derivations are presented.

II. METALS DESCRIBED BY THE PLASMA MODEL

The free energy per unit area of a free-standing metallic film of thickness a in vacuum at temperature T in thermal equilibrium with an environment is given by the Lifshitz formula [2,3]:

$$\mathcal{F}(a, T) = \frac{k_B T}{2\pi} \sum_{l=0}^{\infty} \int_0^{\infty} k_{\perp} dk_{\perp} \times \sum_{\alpha} \ln [1 - r_{\alpha}^2(i\xi_l, k_{\perp}) e^{-2ak(i\xi_l, k_{\perp})}]. \quad (1)$$

Here k_B is the Boltzmann constant, k_{\perp} is the magnitude of the projection of the wave vector on the film plane, $\xi_l = 2\pi k_B T l / \hbar$, $l = 0, 1, 2, \dots$ are the Matsubara frequencies, the prime on the summation sign multiplies the term with $l = 0$ by $1/2$, and

$$k(i\xi_l, k_{\perp}) = \sqrt{k_{\perp}^2 + \varepsilon_l \frac{\xi_l^2}{c^2}}, \quad (2)$$

where $\varepsilon_l \equiv \varepsilon(i\xi_l)$ is the frequency-dependent dielectric permittivity of film metal calculated at the pure imaginary Matsubara frequencies.

The reflection coefficients for two independent polarizations of the electromagnetic field, transverse magnetic ($\alpha = \text{TM}$) and transverse electric ($\alpha = \text{TE}$), are given by

$$r_{\text{TM}}(i\xi_l, k_{\perp}) = \frac{k(i\xi_l, k_{\perp}) - \varepsilon_l q(i\xi_l, k_{\perp})}{k(i\xi_l, k_{\perp}) + \varepsilon_l q(i\xi_l, k_{\perp})},$$

$$r_{\text{TE}}(i\xi_l, k_{\perp}) = \frac{k(i\xi_l, k_{\perp}) - q(i\xi_l, k_{\perp})}{k(i\xi_l, k_{\perp}) + q(i\xi_l, k_{\perp})}, \quad (3)$$

where

$$q(i\xi_l, k_{\perp}) = \sqrt{k_{\perp}^2 + \frac{\xi_l^2}{c^2}}. \quad (4)$$

Equation (1) is obtained [14] from the standard Lifshitz formula for a three-layer system [39–41], where the metallic plate is sandwiched between two vacuum semispaces. Note that the reflection coefficients (3) have the opposite sign, as compared to the case of two plates separated by the vacuum gap [2]. The reason is that here an incident wave inside the film material goes to its boundary plane with a vacuum, and not from the vacuum gap to the material boundary. Another distinctive feature of Eq. (1) from the standard Lifshitz formula is that here the dielectric permittivity of metal enters the power of the exponent [in the standard case this exponent contains the quantity q defined in Eq. (4)]. This makes the properties of the free energy (1) quite different from those in the case of two parallel plates separated by a vacuum gap.

It is convenient to introduce the dimensionless integration variable

$$y = 2aq(i\xi_l, k_{\perp}). \quad (5)$$

Using the characteristic frequency $\omega_c \equiv c/(2a)$, we also pass on the dimensionless Matsubara frequencies:

$$\zeta_l = \frac{\xi_l}{\omega_c} = 4\pi \frac{k_B T a}{\hbar c} l \equiv \tau l. \quad (6)$$

Then the Casimir free energy (1) takes the form

$$\begin{aligned} \mathcal{F}(a, T) &= \frac{k_B T}{8\pi a^2} \sum_{l=0}^{\infty} \int_{\zeta_l}^{\infty} y dy \\ &\times \sum_{\alpha} \ln [1 - r_{\alpha}^2(i\zeta_l, y) e^{-\sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2}}]. \end{aligned} \quad (7)$$

In terms of the quantities (5) and (6), the reflection coefficients (3) are given by

$$\begin{aligned} r_{\text{TM}}(i\zeta_l, y) &= \frac{\sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2} - \varepsilon_l y}{\sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2} + \varepsilon_l y}, \\ r_{\text{TE}}(i\zeta_l, y) &= \frac{\sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2} - y}{\sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2} + y}. \end{aligned} \quad (8)$$

Now we assume that at the imaginary Matsubara frequencies the film metal is described by the lossless plasma model

$$\varepsilon_{l,p} = 1 + \frac{\omega_p^2}{\zeta_l^2}, \quad (9)$$

where ω_p is the plasma frequency. In terms of dimensionless frequencies (6), the dielectric permittivity (9) takes the form

$$\varepsilon_{l,p} = 1 + \frac{\tilde{\omega}_p^2}{\zeta_l^2}, \quad \tilde{\omega}_p \equiv \frac{\omega_p}{\omega_c} = \frac{2a\omega_p}{c}. \quad (10)$$

Substituting Eq. (10) in Eq. (8), one obtains the reflection coefficients in the case when the plasma model is used:

$$\begin{aligned} r_{\text{TM},p}(i\zeta_l, y) &= \frac{\zeta_l^2 (\sqrt{y^2 + \tilde{\omega}_p^2} - y) - \tilde{\omega}_p^2 y}{\zeta_l^2 (\sqrt{y^2 + \tilde{\omega}_p^2} + y) + \tilde{\omega}_p^2 y}, \\ r_{\text{TE},p}(i\zeta_l, y) &= r_{\text{TE},p}(y) = \frac{\sqrt{y^2 + \tilde{\omega}_p^2} - y}{\sqrt{y^2 + \tilde{\omega}_p^2} + y}. \end{aligned} \quad (11)$$

For the film described by the plasma model, it is convenient to rewrite the Casimir free energy (7) as

$$\begin{aligned} \mathcal{F}_p(a, T) &= \frac{k_B T}{8\pi a^2} \sum_{l=0}^{\infty} \Phi(\zeta_l) \\ &= \frac{k_B T}{8\pi a^2} \sum_{l=0}^{\infty} [\Phi_{\text{TM}}(\zeta_l) + \Phi_{\text{TE}}(\zeta_l)], \end{aligned} \quad (12)$$

where

$$\Phi_{\text{TM(TE)}}(x) = \int_x^{\infty} y dy \ln [1 - r_{\text{TM(TE),p}}^2(ix, y) e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}]. \quad (13)$$

It is well known that the Casimir free energy can be presented in the form

$$\mathcal{F}_p(a, T) = E_p(a, T) + \Delta_T \mathcal{F}_p(a, T), \quad (14)$$

where the Casimir energy per unit area at zero temperature is given by [2,3]

$$E_p(a, T) = \frac{\hbar c}{32\pi^2 a^3} \int_0^{\infty} d\zeta \Phi(\zeta), \quad (15)$$

and $\Delta_T \mathcal{F}_p$ is the thermal correction to it.

Applying the Abel-Plana formula to Eq. (12) and taking into account that $\zeta_l = \tau l$, one arrives at

$$\Delta_T \mathcal{F}_p(a, T) = i \frac{k_B T}{8\pi a^2} \int_0^{\infty} dt \frac{\Phi(i\tau t) - \Phi(-i\tau t)}{e^{2\pi t} - 1}. \quad (16)$$

It is evident that the low-temperature behavior of the Casimir free energy of thin metallic films can be found from the perturbation expansion of Eq. (16) under the condition $\tau t \ll 1$. In doing so, it is convenient to consider the contributions of the TM and TE modes to Eq. (16) separately taking into account Eq. (12). Note that for two media with a gap between of them the low temperature expansion in the Lifshitz formula was performed in Refs. [32–36]. These results were systemized and partly extended in Ref. [42].

We start from the TE mode because in this case the function under the integral in Eq. (13) does not depend on x due to the second equality in Eq. (11). This means that the total dependence of $\Phi_{\text{TE}}(x)$ on x is determined by only the lower integration limit in Eq. (13).

Now we expand the function $\Phi_{\text{TE}}(x)$ in a series in powers of x . The first term in this series is

$$\Phi_{\text{TE}}(0) = \int_0^{\infty} y dy \ln [1 - r_{\text{TE},p}^2(y) e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}]. \quad (17)$$

This is a converging integral, which does not contribute to the difference:

$$\Delta \Phi_{\text{TE}} \equiv \Phi_{\text{TE}}(i\tau t) - \Phi_{\text{TE}}(-i\tau t), \quad (18)$$

appearing in Eq. (16). Then, calculating the first and second derivatives of Eq. (13), one finds

$$\Phi'_{\text{TE}}(0) = 0, \quad \Phi''_{\text{TE}}(0) = -\ln(1 - e^{-\tilde{\omega}_p}). \quad (19)$$

The respective terms of the power series again do not contribute to the difference (18).

Finally, we find

$$\Phi'''_{\text{TE}}(0) = -\frac{8}{\tilde{\omega}_p} \frac{1}{e^{\tilde{\omega}_p} - 1}, \quad (20)$$

and, thus,

$$\begin{aligned} \Phi_{\text{TE}}(x) &= \Phi_{\text{TE}}(0) - \frac{x^2}{2} \ln(1 - e^{-\tilde{\omega}_p}) \\ &\quad - \frac{4}{3\tilde{\omega}_p} \frac{x^3}{e^{\tilde{\omega}_p} - 1} + O(x^4), \end{aligned} \quad (21)$$

where $\Phi_{\text{TE}}(0)$ is defined in Eq. (17).

Restricting ourselves by the third perturbation order, Eqs. (18) and (21) result in

$$\Delta \Phi_{\text{TE}} \approx i \frac{8}{3\tilde{\omega}_p} \frac{\tau^3 t^3}{e^{\tilde{\omega}_p} - 1}. \quad (22)$$

We come now to the contribution of the TM mode to the quantity (16). This case is more complicated because both the lower integration limit and the function under the integral in Eq. (13) depend on x .

By calculating several first derivatives of Eq. (13), where the reflection coefficient is defined by the first equality in Eq. (11), one finds

$$\begin{aligned}\Phi_{\text{TM}}(0) &= \int_0^\infty y dy \ln(1 - e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}), \\ \Phi'_{\text{TM}}(0) &= 0, \\ \Phi''_{\text{TM}}(0) &= \frac{8}{\tilde{\omega}_p^2} \int_0^\infty dy \frac{\sqrt{y^2 + \tilde{\omega}_p^2}}{e^{\sqrt{y^2 + \tilde{\omega}_p^2}} - 1} - \ln(1 - e^{-\tilde{\omega}_p}), \\ \Phi'''_{\text{TM}}(0) &= -\frac{16}{\tilde{\omega}_p} \frac{1}{e^{\tilde{\omega}_p} - 1}.\end{aligned}\quad (23)$$

It is evident that the first two terms in the power series, defined by Eq. (23),

$$\Phi_{\text{TM}}(x) = \Phi_{\text{TM}}(0) + \frac{\Phi''_{\text{TM}}(0)x^2}{2} - \frac{8}{3\tilde{\omega}_p} \frac{x^3}{e^{\tilde{\omega}_p} - 1} + O(x^4),\quad (24)$$

do not contribute to the quantity

$$\Delta\Phi_{\text{TM}} \equiv \Phi_{\text{TM}}(i\tau t) - \Phi_{\text{TM}}(-i\tau t).\quad (25)$$

Then, restricting ourselves by the third perturbation order, we arrive at

$$\Delta\Phi_{\text{TM}} \approx i \frac{16}{3\tilde{\omega}_p} \frac{\tau^3 t^3}{e^{\tilde{\omega}_p} - 1}.\quad (26)$$

By summing Eqs. (22) and (26), one obtains

$$\Phi(i\tau t) - \Phi(-i\tau t) = \Delta\Phi_{\text{TM}} + \Delta\Phi_{\text{TE}} \approx i \frac{8}{\tilde{\omega}_p} \frac{\tau^3 t^3}{e^{\tilde{\omega}_p} - 1}.\quad (27)$$

Substituting this result in Eq. (16), integrating with respect to t and returning to the dimensional variables, we find the behavior of the thermal correction to the Casimir energy of metallic film at low temperature:

$$\Delta_T \mathcal{F}_p(a, T) = -\frac{2\pi^2(k_B T)^4}{15\hbar^3 c^2 \omega_p (e^{2a\omega_p/c} - 1)}.\quad (28)$$

The respective thermal correction to the Casimir pressure of a free-standing metallic film at low T takes the form

$$\Delta_T P_p(a, T) = -\frac{\partial \mathcal{F}_p(a, T)}{\partial a} = -\frac{4\pi^2(k_B T)^4}{15\hbar^3 c^3} \frac{e^{2a\omega_p/c}}{(e^{2a\omega_p/c} - 1)^2}.\quad (29)$$

An interesting feature of Eqs. (28) and (29) is that the thermal corrections to the Casimir energy and pressure of metallic film, calculated using the plasma model, go to zero exponentially fast with increasing film thickness a . Thus, there is no classical limit in this case.

Another important point is that for fixed film thickness the Casimir free energy and pressure of the film go to zero in the limiting case $\omega_p \rightarrow \infty$. This is true for both the thermal corrections (28) and (29) and for the zero-temperature quantities $E(a)$ and $P(a)$. Note that for $\omega_p \rightarrow \infty$ the magnitudes of both the TM and TE reflection coefficients (11) go to unity, i.e., the

film becomes perfectly reflecting. One can conclude that when the plasma model is used in calculations an ideal metal film is characterized by the zero Casimir energy and pressure, as it should be because the electromagnetic fluctuations cannot penetrate an interior of ideal metal.

From Eq. (28) one can also obtain the low-temperature behavior of the Casimir entropy of metallic film:

$$S_p(a, T) = -\frac{\partial \mathcal{F}_p(a, T)}{\partial T} = \frac{8\pi^2 k_B (k_B T)^3}{15\hbar^3 c^2 \omega_p (e^{2a\omega_p/c} - 1)}.\quad (30)$$

It is seen that the Casimir entropy of a film is positive. When the temperature vanishes, one has from Eq. (30)

$$S_p(a, T) \rightarrow 0;\quad (31)$$

i.e., the Casimir entropy of metallic film calculated using the plasma model satisfies the Nernst heat theorem.

In the end of this section, we discuss the application region of asymptotic Eqs. (28)–(30), which were derived under a condition $x \ll 1$, i.e., $\tau t \ll 1$. Taking into account that the dominant contribution to the integral (16) is given by $t \sim 1/(2\pi)$ and considering the definition of τ in Eq. (6), one rewrites the application condition in the form

$$k_B T \ll \frac{\hbar c}{2a} = \hbar \omega_c.\quad (32)$$

For a typical film thickness $a = 100$ nm, this inequality results in $T \ll 11\,400$ K, i.e., Eqs. (28)–(30) are well applicable under a condition $T \leq 1000$ K. With increasing film thickness the application region of Eqs. (28)–(30) becomes more narrow. For example, for $a = 1$ μm these equations are applicable at $T \leq 100$ K.

III. METALS DESCRIBED BY THE DRUDE MODEL

Now we describe metal of the film by the Drude model, which takes into account the relaxation properties of conduction electrons. At the pure imaginary Matsubara frequencies the dielectric permittivity of the Drude metal takes the form

$$\varepsilon_{l,D} = 1 + \frac{\omega_p^2}{\xi_l[\xi_l + \gamma(T)]},\quad (33)$$

where $\gamma(T)$ is the temperature-dependent relaxation parameter.

Using the dimensionless variables (6) and (10) and introducing the dimensionless relaxation parameter,

$$\tilde{\gamma}(T) = \frac{\gamma(T)}{\omega_c},\quad (34)$$

Eq. (33) can be rewritten as

$$\varepsilon_{l,D} = 1 + \frac{\tilde{\omega}_p^2}{\zeta_l[\zeta_l + \tilde{\gamma}(T)]}.\quad (35)$$

It is convenient also to introduce one more dimensionless parameter,

$$\delta_l(T) = \frac{\tilde{\gamma}(T)}{\zeta_l} = \frac{\gamma(T)}{\xi_l} = \frac{\hbar\gamma(T)}{2\pi k_B T} \frac{1}{l},\quad (36)$$

where $l \geq 1$.

It is easily seen that for metals with perfect crystal lattices this parameter satisfies a condition

$$\delta_l(T) \ll 1, \quad (37)$$

and becomes progressively smaller with decreasing temperature. Thus, at $T = 300$ K for good metals we have $\gamma \sim 10^{13}$ rad/s (for Au $\gamma = 5.3 \times 10^{13}$ rad/s), whereas $\xi_1 = 2.5 \times 10^{14}$ rad/s. In the temperature region $T_D/4 < T < 300$ K, where T_D is the Debye temperature (for Au we have $T_D = 165$ K [43]), it holds $\gamma(T) \sim T$, i.e., the value of δ_l remains unchanged. In the region from $T_D/4$ down to liquid helium temperature $\gamma(T) \sim T^5$ in accordance to the Bloch-Grüneisen law [44] and at lower temperatures $\gamma(T) \sim T^2$ for metals with perfect crystal lattices [43]. As a result, even the quantity $\delta_1(T)$ and, all the more, $\delta_l(T)$ go to zero when T vanishes. For example, for Au at $T = 30$ and 10 K one has $\delta_1 \approx 5 \times 10^{-2}$ and 2×10^{-3} , respectively.

Now we express the permittivity (35) in terms of the small parameter (37)

$$\varepsilon_{l,D} = 1 + \frac{\tilde{\omega}_p^2}{\zeta_l^2 [1 + \delta_l(T)]} \quad (38)$$

and, in the first perturbation order in this parameter, obtain

$$\varepsilon_{l,D} \approx \varepsilon_{l,p} - \frac{\tilde{\omega}_p^2}{\zeta_l^2} \delta_l(T). \quad (39)$$

We next use the following identical representation for the Casimir free energy of metallic film calculated using the Drude model:

$$\mathcal{F}_D(a, T) = \mathcal{F}_p(a, T) + \mathcal{F}_D^{(0)}(a, T) - \mathcal{F}_p^{(0)}(a, T) + \mathcal{F}^{(\gamma)}(a, T). \quad (40)$$

Here \mathcal{F}_p is the free energy (12) calculated using the plasma model and $\mathcal{F}_p^{(0)}$ is its zero-frequency term

$$\begin{aligned} \mathcal{F}_p^{(0)}(a, T) &= \frac{k_B T}{16\pi a^2} \int_0^\infty y dy \{ \ln(1 - e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}) \\ &\quad + \ln[1 - r_{\text{TE},p}^2(y) e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}] \}, \end{aligned} \quad (41)$$

where the reflection coefficient $r_{\text{TE},p}$ is defined in the second line of Eq. (11).

The quantity $\mathcal{F}_D^{(0)}$ in Eq. (40) is the zero-frequency term in the Casimir free energy of a film when the Drude model is used in calculations. From Eqs. (7) and (8) one obtains

$$\begin{aligned} \mathcal{F}_D^{(0)}(a, T) &= \frac{k_B T}{16\pi a^2} \int_0^\infty y dy \ln(1 - e^{-y}) \\ &= -\frac{k_B T}{16\pi a^2} \zeta(3), \end{aligned} \quad (42)$$

where $\zeta(z)$ is the Riemann zeta function.

Finally, the quantity $\mathcal{F}^{(\gamma)}$ in Eq. (40) is the difference of all nonzero-frequency Matsubara terms in the Casimir free energy (7) calculated using the Drude and plasma models:

$$\begin{aligned} \mathcal{F}^{(\gamma)}(a, T) &= \frac{k_B T}{8\pi a^2} \sum_{l=1}^\infty \int_{\zeta_l}^\infty y dy \\ &\quad \times \{ \ln[1 - r_{\text{TM},D}^2(i\zeta_l, y) e^{-\sqrt{y^2 + \tilde{\omega}_p^2(1 - \delta_l)}}] \} \end{aligned}$$

$$\begin{aligned} &+ \ln[1 - r_{\text{TE},D}^2(i\zeta_l, y) e^{-\sqrt{y^2 + \tilde{\omega}_p^2(1 - \delta_l)}}] \\ &- \ln[1 - r_{\text{TM},p}^2(i\zeta_l, y) e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}] \\ &- \ln[1 - r_{\text{TE},p}^2(i\zeta_l, y) e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}] \}. \end{aligned} \quad (43)$$

As shown in the Appendix,

$$\lim_{T \rightarrow 0} \mathcal{F}^{(\gamma)}(a, T) = 0, \quad \lim_{T \rightarrow 0} \frac{\partial \mathcal{F}^{(\gamma)}(a, T)}{\partial T} = 0. \quad (44)$$

Because of this, we concentrate our attention on the other contributions to the right-hand side of Eq. (40).

The quantity \mathcal{F}_p is already found in Eqs. (14) and (28), and the quantity $\mathcal{F}_D^{(0)}$ is presented in Eq. (42). Here we calculate the quantity $\mathcal{F}_p^{(0)}$ defined in Eq. (41). Let us start with the integral

$$I_1(\tilde{\omega}_p) \equiv \int_0^\infty y dy \ln(1 - e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}). \quad (45)$$

Expanding the logarithm in power series and introducing the new integration variable

$$t = n\sqrt{y^2 + \tilde{\omega}_p^2}, \quad (46)$$

one obtains from Eq. (45)

$$\begin{aligned} I_1(\tilde{\omega}_p) &= -\sum_{n=1}^\infty \frac{1}{n^3} \int_{n\tilde{\omega}_p}^\infty t dt e^{-t} \\ &= -\sum_{n=1}^\infty \frac{1}{n^3} (1 + n\tilde{\omega}_p) e^{-n\tilde{\omega}_p}. \end{aligned} \quad (47)$$

After a summation, Eq. (47) results in

$$I_1(\tilde{\omega}_p) = -[\text{Li}_3(e^{-\tilde{\omega}_p}) + \tilde{\omega}_p \text{Li}_2(e^{-\tilde{\omega}_p})], \quad (48)$$

where $\text{Li}_k(z)$ is the polylogarithm function.

Now we consider the second integral entering Eq. (41),

$$I_2(\tilde{\omega}_p) \equiv \int_0^\infty y dy \ln[1 - r_{\text{TE},p}^2(y) e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}], \quad (49)$$

where the reflection coefficient $r_{\text{TE},p}$ is defined in Eq. (11). Note that for physical values of $\tilde{\omega}_p$ the quantity subtracted from unity under the logarithm in Eq. (49) is much smaller than unity. The reason is that if $\tilde{\omega}_p$ is not large the squared reflection coefficient $r_{\text{TE},p}^2$ is rather small. Then one can expand the logarithm up to the first power of this parameter and obtain

$$I_2(\tilde{\omega}_p) \approx -\int_0^\infty y dy r_{\text{TE},p}^2(y) e^{-\sqrt{y^2 + \tilde{\omega}_p^2}}. \quad (50)$$

Numerical computations show that Eqs. (49) and (50) lead to nearly coincident results for $\tilde{\omega}_p \geq 0.5$. Taking into account the definition of $\tilde{\omega}_p$ in Eq. (10), this results in the condition $a \geq 5.4$ nm for a thickness of Au film with $\omega_p = 1.37 \times 10^{16}$ rad/s. This is quite sufficient for our purposes because here we consider metallic films of more than 7 nm thickness, which can be described by the isotropic dielectric permittivity [45] (for thinner Au films the effect of anisotropy should be taken into account [46]).

Now we introduce the variable $t = y/\tilde{\omega}_p$ and, using Eq. (11), identically represent the quantity $r_{\text{TE},p}^2$ in the form

$$r_{\text{TE},p}^2(y) = 1 + 8t^2 + 8t^4 - 4t\sqrt{1+t^2} - 8t^2\sqrt{1+t^2}. \quad (51)$$

Introducing the integration variable t in Eq. (50), one finds

$$I_2(\tilde{\omega}_p) \approx -\tilde{\omega}_p^2 \int_0^\infty t dt e^{-\tilde{\omega}_p \sqrt{1+t^2}} (1 + 8t^2 + 8t^4 - 4t\sqrt{1+t^2} - 8t^2\sqrt{1+t^2}). \quad (52)$$

Calculating all the five integrals in Eq. (52) [47], we arrive at

$$I_2(\tilde{\omega}_p) \approx -\left(\tilde{\omega}_p + 17 + \frac{112}{\tilde{\omega}_p} + \frac{432}{\tilde{\omega}_p^2} + \frac{960}{\tilde{\omega}_p^3} + \frac{960}{\tilde{\omega}_p^4}\right) e^{-\tilde{\omega}_p} + 4\left[\tilde{\omega}_p K_1(\tilde{\omega}_p) + 9K_2(\tilde{\omega}_p) + \frac{30}{\tilde{\omega}_p} K_3(\tilde{\omega}_p)\right]. \quad (53)$$

As a result, the Casimir free energy (40), calculated using the Drude model, can be rewritten in the form

$$\mathcal{F}_D(a, T) = \mathcal{F}_p(a, T) + \mathcal{F}^{(\nu)}(a, T) - \frac{k_B T}{16\pi a^2} \left[\zeta(3) + I_1\left(\frac{2a\omega_p}{c}\right) + I_2\left(\frac{2a\omega_p}{c}\right) \right], \quad (54)$$

where \mathcal{F}_p and $\mathcal{F}^{(\nu)}$ are presented in Eqs. (14), (28), (43), and I_1 and I_2 are found in Eqs. (48) and (53).

Now we calculate the negative derivative of Eq. (54) with respect to T and find the limiting value of this derivative when T goes to zero using Eqs. (28) and (44). The result is

$$S_D(a, 0) = \frac{k_B}{16\pi a^2} \left[\zeta(3) + I_1\left(\frac{2a\omega_p}{c}\right) + I_2\left(\frac{2a\omega_p}{c}\right) \right]. \quad (55)$$

As is seen in Eq. (55), the Casimir entropy of metallic film at zero temperature, calculated using the Drude model, is not equal to zero and depends on the parameters of a film (the thickness a and the plasma frequency ω_p). Thus, in this case the Nernst heat theorem is violated [37,38].

Calculations using Eqs. (48) and (53) show that

$$S_D(a, 0) > 0. \quad (56)$$

Thus, for $\tilde{\omega}_p = 1$ (i.e., for a Au film of approximately 11 nm thickness) one has $I_1 = -0.79575$, $I_2 = -0.02456$, which leads to the number in square brackets in Eq. (55) $C = 0.38175$. For $\tilde{\omega}_p = 5$ ($a = 55$ nm) the respective results are $I_1 = -0.04049$, $I_2 = -0.006684$, and $C = 1.15489$. Finally, for $\tilde{\omega}_p = 15$ ($a = 165$ nm) $I_1 = -4.894 \times 10^{-6}$, $I_2 = -1.5966 \times 10^{-6}$, and $C = 1.20205$. We see that with increasing film thickness the magnitudes of the quantities I_1 and I_2 become negligibly small, as compared with $\zeta(3)$.

IV. CONCLUSIONS AND DISCUSSION

In the foregoing, we have considered the low-temperature behavior of the Casimir free energy, entropy, and pressure of metallic films in vacuum. It was shown that the calculation results are quite different depending on whether the plasma or the Drude model is used to describe the dielectric response of a film metal. If the lossless plasma model is used, as is suggested by the results of several precise experiments on measuring the Casimir force, we have obtained explicit analytic expressions for the thermal corrections to the Casimir energy and pressure and for the Casimir entropy of a film, which are applicable over the wide temperature region down to zero temperature.

These expressions do not have a classical limit and go to zero when the film material becomes perfectly reflecting. The Casimir entropy is shown to be positive and satisfying the Nernst heat theorem; i.e., it goes to zero in the limiting case of zero temperature.

If the film metal is described by the Drude model taking into account the relaxation properties of conduction electrons at low frequencies, the calculation results are quite different, both qualitatively and quantitatively. In accordance to what was shown in previous work [14–16], the Casimir free energy and pressure reach the classical limit for rather thin metallic films of approximately 150 nm thickness. However, in contradiction to physical intuition, the Casimir free energy does not go to zero in the limiting case of ideal metal film.

We have found analytically the Casimir entropy of metallic films with perfect crystal lattices, described by the Drude model, at zero temperature. It is demonstrated that this quantity takes a positive value depending on the parameters of a film, i.e., the Nernst heat theorem is violated. Thus, the case of a free-standing film is different from the case of two nonmagnetic metal plates described by the Drude model interacting through a vacuum gap. In the latter case the Nernst heat theorem is also violated if the Drude model is used in calculations, but the Casimir entropy takes a negative value at $T = 0$ [32–34].

The obtained results raise a problem on what is the proper way to calculate the dispersion-force contribution to the free energy of metallic films. As discussed in Sec. I, the resolution of this problem is important for investigations of stability of thin films. Previous precise experiments on measuring the Casimir force between metallic test bodies [17–23,27,28] have always been found in agreement with theoretical predictions of the thermodynamically consistent approach using the plasma model and excluded the theoretical predictions obtained using the Drude model. Recently it was shown [48] that theoretical description of the Casimir interaction in graphene systems by means of the polarization tensor, which is in agreement [49] with the experimental data [50], also satisfies the Nernst heat theorem. Thus, there is good reason to suppose that the contribution of dispersion forces to the free energy of metallic films should also be calculated in a thermodynamically consistent way, i.e., using the plasma model. An experimental confirmation to this hypothesis might be expected within the next few years.

ACKNOWLEDGMENT

The work of V.M.M. was partially supported by the Russian Government Program of Competitive Growth of Kazan Federal University.

APPENDIX

Here we investigate the low-temperature behavior of the quantity $\mathcal{F}^{(\nu)}$ defined in Eq. (43) and prove Eq. (44) used in Sec. III. For this purpose we expand $\mathcal{F}^{(\nu)}$ up to the first order in small parameter $\delta_i(T)$ defined in Eq. (36). According to the results of Sec. III, for metals with perfect crystal lattices this parameter becomes progressively smaller with decreasing T .

The reflection coefficients in the case when the Drude model is used can be obtained by substituting Eq. (39) in Eq. (8):

$$\begin{aligned} r_{\text{TM},D}(i\zeta_l, y) &\approx \frac{\sqrt{y^2 + (\varepsilon_{l,p} - 1)\zeta_l^2 - \tilde{\omega}_p^2 \delta_l} - \varepsilon_{l,p} y + \frac{\tilde{\omega}_p^2 y}{\zeta_l^2} \delta_l}{\sqrt{y^2 + (\varepsilon_{l,p} - 1)\zeta_l^2 - \tilde{\omega}_p^2 \delta_l} + \varepsilon_{l,p} y - \frac{\tilde{\omega}_p^2 y}{\zeta_l^2} \delta_l}, \\ r_{\text{TE},D}(i\zeta_l, y) &\approx \frac{\sqrt{y^2 + (\varepsilon_{l,p} - 1)\zeta_l^2 - \tilde{\omega}_p^2 \delta_l} - y}{\sqrt{y^2 + (\varepsilon_{l,p} - 1)\zeta_l^2 - \tilde{\omega}_p^2 \delta_l} + y}. \end{aligned} \quad (\text{A1})$$

Expanding the second powers of these coefficients up to the first order of $\delta_l = \delta_l(T)$, one obtains

$$\begin{aligned} r_{\text{TM},D}^2(i\zeta_l, y) &\approx r_{\text{TM},p}^2(i\zeta_l, y) - \delta_l(T) R_{\text{TM}}(i\zeta_l, y), \\ r_{\text{TE},D}^2(i\zeta_l, y) &\approx r_{\text{TE},p}^2(i\zeta_l, y) - \delta_l(T) R_{\text{TE}}(i\zeta_l, y), \end{aligned} \quad (\text{A2})$$

where the quantities R_{TM} and R_{TE} are given by

$$\begin{aligned} R_{\text{TM}}(i\zeta_l, y) &= \frac{2\tilde{\omega}_p^2 \zeta_l^2 y (\tilde{\omega}_p^2 + 2y^2 - \zeta_l^2) (\tilde{\omega}_p^2 y + \zeta_l^2 y - \zeta_l^2 \sqrt{y^2 + \tilde{\omega}_p^2})}{\sqrt{y^2 + \tilde{\omega}_p^2} (\tilde{\omega}_p^2 y + \zeta_l^2 y + \zeta_l^2 \sqrt{y^2 + \tilde{\omega}_p^2})^3}, \\ R_{\text{TE}}(i\zeta_l, y) = R_{\text{TE}}(y) &= \frac{2\tilde{\omega}_p^2 y (\sqrt{y^2 + \tilde{\omega}_p^2} - y)}{\sqrt{y^2 + \tilde{\omega}_p^2} (\sqrt{y^2 + \tilde{\omega}_p^2} + y)^3}. \end{aligned} \quad (\text{A3})$$

It is easily seen that for any $y \geq \zeta_l$ it holds $R_{\text{TM}} > 0$ and $R_{\text{TE}} > 0$.

Now we consider the exponential factor in the first two contributions to Eq. (43). Up to the first order in δ_l , this factor can be presented in the form

$$\begin{aligned} e^{-\sqrt{y^2 + \tilde{\omega}_p^2} (1 - \delta_l)} &= e^{-\sqrt{y^2 + \tilde{\omega}_p^2} \sqrt{1 - \frac{\delta_l \tilde{\omega}_p^2}{y^2 + \tilde{\omega}_p^2}}} \\ &\approx e^{-\sqrt{y^2 + \tilde{\omega}_p^2} \left[1 - \frac{\delta_l \tilde{\omega}_p^2}{2(y^2 + \tilde{\omega}_p^2)}\right]}. \end{aligned} \quad (\text{A4})$$

Next we use the fact that not only δ_l , but also $\delta_l \tilde{\omega}_p / 2$ is the small parameters at sufficiently low temperature. Really, in accordance to Eq. (36), the largest value of this parameter is

$$\delta_1 \frac{\tilde{\omega}_p}{2} = \frac{\gamma}{\xi_1} \frac{a \omega_p}{c}. \quad (\text{A5})$$

For Au at $T = 10$ K we have $\gamma / \xi_1 \approx 2 \times 10^{-3}$, so that the quantity (A5) does not exceed 0.2 for film thicknesses $a \leq 2 \mu\text{m}$. At $T = 5$ K the parameter (A5) does not exceed 0.2 for Au films with $a \leq 20 \mu\text{m}$ thickness.

Expanding the right-hand side of Eq. (A4) up to the first order in parameter $\delta_l \tilde{\omega}_p / 2$, we obtain

$$e^{-\sqrt{y^2 + \tilde{\omega}_p^2} (1 - \delta_l)} \approx e^{-\sqrt{y^2 + \tilde{\omega}_p^2}} \left(1 + \delta_l \frac{\tilde{\omega}_p^2}{2\sqrt{y^2 + \tilde{\omega}_p^2}}\right). \quad (\text{A6})$$

Substituting Eqs. (A2) and (A6) in Eq. (43), expanding the first two logarithms in powers of δ_l and preserving only the terms of the first order, one arrives at

$$\mathcal{F}^{(\gamma)}(a, T) \approx -\frac{k_B T}{8\pi a^2} \sum_{l=1}^{\infty} \delta_l(t) \int_{\zeta_l}^{\infty} y dy \left[\frac{Q_{\text{TM}}(i\zeta_l, y)}{e^{\sqrt{y^2 + \tilde{\omega}_p^2}} - r_{\text{TM},p}^2(i\zeta_l, y)} + \frac{Q_{\text{TE}}(i\zeta_l, y)}{e^{\sqrt{y^2 + \tilde{\omega}_p^2}} - r_{\text{TE},p}^2(i\zeta_l, y)} \right]. \quad (\text{A7})$$

Here we have introduced the notations

$$\begin{aligned} Q_{\text{TM}}(i\zeta_l, y) &= \frac{\tilde{\omega}_p^2}{2\sqrt{y^2 + \tilde{\omega}_p^2}} - R_{\text{TM}}(i\zeta_l, y), \\ Q_{\text{TE}}(i\zeta_l, y) = Q_{\text{TE}}(y) &= \frac{\tilde{\omega}_p^2}{2\sqrt{y^2 + \tilde{\omega}_p^2}} - R_{\text{TE}}(y), \end{aligned} \quad (\text{A8})$$

and the quantities R_{TM} and R_{TE} are defined in Eq. (A3).

It is easily seen that $Q_{\text{TM}} > 0$ and $Q_{\text{TE}} > 0$, so that $\mathcal{F}^{(\nu)}(a, T) < 0$. This is because the magnitude of the Casimir free energy of a film described by the Drude model is larger than that of a film described by the plasma model (as opposed to the case of metallic plates separated with a vacuum gap [34]).

Equation (A7) can be used to prove the validity of Eq. (44). For this purpose we increase the magnitude of the right-hand side of Eq. (A7) by replacing $r_{\text{TM(TE),p}}^2$ with unities in the denominators, and by omitting the quantities $R_{\text{TM(TE)}}$ in Eq. (A8) for the numerators. Using also the definition of δ_l in Eq. (36), and the definition of $\tilde{\omega}_p$ from Eq. (10) in the prefactor, one obtains

$$|\mathcal{F}^{(\nu)}(a, T)| < \frac{\hbar\gamma(T)\omega_p^2}{4\pi^2c^2} \sum_{l=1}^{\infty} \frac{1}{l} \int_{\zeta_l}^{\infty} \frac{y dy}{\sqrt{y^2 + \tilde{\omega}_p^2}} \frac{1}{e^{\sqrt{y^2 + \tilde{\omega}_p^2}} - 1}. \quad (\text{A9})$$

Now we introduce the new variable $t = \sqrt{y^2 + \tilde{\omega}_p^2}$ and expanding in powers of e^{-t} find

$$|\mathcal{F}^{(\nu)}(a, T)| < \frac{\hbar\gamma(T)\omega_p^2}{4\pi^2c^2} \sum_{n=1}^{\infty} \sum_{l=1}^{\infty} \frac{1}{l} \int_{\sqrt{\zeta_l^2 + \tilde{\omega}_p^2}}^{\infty} dt e^{-nt}. \quad (\text{A10})$$

Calculating the integral and using the inequality

$$\frac{\zeta_l + \tilde{\omega}_p}{\sqrt{2}} < \sqrt{\zeta_l^2 + \tilde{\omega}_p^2}, \quad (\text{A11})$$

we arrive at

$$|\mathcal{F}^{(\nu)}(a, T)| < \frac{\hbar\gamma(T)\omega_p^2}{4\pi^2c^2} \sum_{n=1}^{\infty} \frac{1}{n} \sum_{l=1}^{\infty} \frac{1}{l} e^{-n\frac{\tilde{\omega}_p + \zeta_l}{\sqrt{2}}}. \quad (\text{A12})$$

Taking into account that $\zeta_l = \tau l$, we perform a summation with respect to l and obtain

$$|\mathcal{F}^{(\nu)}(a, T)| < -\frac{\hbar\gamma(T)\omega_p^2}{4\pi^2c^2} \sum_{n=1}^{\infty} \frac{1}{n} e^{-n\frac{\tilde{\omega}_p}{\sqrt{2}}} \ln(1 - e^{-n\frac{\tau}{\sqrt{2}}}), \quad (\text{A13})$$

where, due to a smallness of τ ,

$$\ln(1 - e^{-n\frac{\tau}{\sqrt{2}}}) \approx \ln\left(n\frac{\tau}{\sqrt{2}}\right) = \ln\tau + \ln n - \frac{1}{2}\ln 2. \quad (\text{A14})$$

Substituting Eq. (A13) in Eq. (A12), we represent the final results in the form

$$|\mathcal{F}^{(\nu)}(a, T)| < X(a, T), \quad (\text{A15})$$

where

$$X(a, T) = \frac{\hbar\gamma(T)\omega_p^2}{4\pi^2c^2} \left(C_1 \ln \frac{4\pi k_B T a}{\hbar c} - C_2 \right), \quad (\text{A16})$$

and the following independent on T coefficients are introduced:

$$C_1 = -\sum_{n=1}^{\infty} \frac{1}{n} e^{-n\frac{\tilde{\omega}_p}{\sqrt{2}}} = \ln(1 - e^{-\frac{\tilde{\omega}_p}{\sqrt{2}}}),$$

$$C_2 = \sum_{n=1}^{\infty} \frac{2\ln n - \ln 2}{2n} e^{-n\frac{\tilde{\omega}_p}{\sqrt{2}}}. \quad (\text{A17})$$

Note that the second series is converging, as well as the first one.

Taking into account that for metals with perfect crystal lattices at very low temperature $\gamma(T) \sim T^2$ (see Sec. III), one concludes from Eq. (A16) that $X(a, T) \rightarrow 0$ when $T \rightarrow 0$. Then, from Eq. (A15), one obtains the first equality in Eq. (44).

From Eq. (A16) it is seen that not only $X(a, 0) = 0$, but

$$\left. \frac{\partial X(a, T)}{\partial T} \right|_{T=0} = 0 \quad (\text{A18})$$

as well. Using Eqs. (A15) and (A18), one easily proves that the second equality in Eq. (44) is valid.

To end, it is pertinent to note that the above results, including Eq. (44), are also valid under a slower vanishing of the relaxation parameter with temperature according to $\gamma(T) \sim T^\beta$ where $\beta > 1$.

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