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Nernst heat theorem for an atom interacting with graphene: Dirac model with nonzero energy gap and chemical potential

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We derive the low-temperature behavior of the Casimir-Polder free energy for a polarizable atom interacting with graphene sheet which possesses the nonzero energy gap Δ and chemical potential μ. The response of graphene to the electromagnetic field is described by means of the polarization tensor in the framework of the Dirac model on the basis of first principles of thermal quantum field theory in the Matsubara formulation. It is shown that the thermal correction to the Casimir-Polder energy consists of three contributions. The first of them is determined by the Matsubara summation using the polarization tensor defined at zero temperature, whereas the second and third contributions are caused by an explicit temperature dependence of the polarization tensor and originate from the zero-frequency Matsubara term and the sum of all Matsubara terms with nonzero frequencies, respectively. The asymptotic behavior for each of the three contributions at low temperature is found analytically for any value of the energy gap and chemical potential. According to our results, the Nernst heat theorem for the Casimir-Polder free energy and entropy is satisfied for both $\Delta > 2\mu$ and $\Delta < 2\mu$. We also reveal an entropic anomaly arising in the case $\Delta = 2\mu$. The obtained results are discussed in connection with the long-standing fundamental problem in Casimir physics regarding the proper description of the dielectric response of matter to the electromagnetic field.

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I. INTRODUCTION

At the moment there is a strong interest in theoretical and experimental investigations of the Casimir [1] and Casimir-Polder [2] forces which act between electrically neutral bodies spaced at short separations one from the other. These forces are of entirely quantum nature and are caused by the zero-point and thermal fluctuations of the electromagnetic field. At separations exceeding several nanometers the Casimir force, which acts between two macroscopic bodies, and the Casimir-Polder force, acting between an atom and a material surface, are of relativistic character by depending on both the Planck constant $\hbar$ and the speed of light c. In fact these forces present the relativistic generalization of the familiar van der Waals forces [3], but take on greater significance due to multidisciplinary applications not only in atomic physics [4–12] and condensed matter physics [13–15], but also in quantum field theory [16–18], gravitation and cosmology [19–22], and for constraining predictions of high energy physics, supersymmetry and supergravity [23–28].

A theoretical description of the Casimir and Casimir-Polder forces between real material bodies is based on the semiclassical Lifshitz theory [29,30], which treats the electromagnetic field in the framework of quantum field theory, but uses the classical description of matter by means of some phenomenological response functions (in certain limits one can derive these forces without involving the Lifshitz theory, see, e.g., Refs. [1,2,31]). In the framework of this theory, the Casimir-Polder atom-plate interaction is expressed via the frequency dependent atomic polarizability and the dielectric permittivity of a plate material. Although the Lifshitz theory was successfully used over a period of several decades, modern precise experiments performed during the past few years revealed serious contradictions between experiment and theory. Specifically, for two metallic bodies the theoretical predictions obtained with taken into account relaxation properties of free (conduction) electrons were found to be in a not so far reconcilable contradiction with the measurement data (see Refs. [32–40] and reviews in Refs. [41–43]). The contradiction arises if the available optical data of a metal are extrapolated down to zero frequency by the well tested Drude model taking the proper account of the relaxation properties of free electrons and dies away if the lossless plasma model is used which should be applicable only at high frequencies.

By an intriguing coincidence, the Casimir entropy, calculated using the Lifshitz theory combined with the Drude model, does not vanish with vanishing temperature for metals with perfect crystal lattices and depends on the volume and other parameters of a system [44–48]. Thus, the Nernst heat theorem, which demands that for a physical system in thermal equilibrium the entropy at zero temperature must either vanish or be equal to the universal constant independent on the system parameters [49,50], is violated in this case. In doing so, the Nernst heat theorem is satisfied if the plasma model is used [44–48] which is consistent with measurements of the Casimir force, but is in conflict with all our knowledge about the electric phenomena occurring at low frequencies. It was noticed also [51–53] that the Casimir entropy jumps to zero at a very low temperature starting from the negative value if the Drude model is used for metals with an imperfect crystal lattice containing some fraction of impurities. This observation, however, does not help to bring the Drude-based theory in agreement with the measurement results for the Casimir force.

A somewhat similar situation was discovered for the Casimir force between two dielectric bodies and for the Casimir-Polder force between a polarizable atom in close proximity to a dielectric plate. It was found that theoretical predictions of the Lifshitz theory obtained with taken into account conductivity at a constant current (dc conductivity) of a dielectric material are in contradiction with the measurement data of Casimir experiments [54–57]. To bring the theoretical predictions in agreement with the measurement data, one needs to omit in computations the really observable dc conductivity of a material [11,54–57]. It seems meaningful that the calculated values of both the Casimir and Casimir-Polder entropies at zero temperature were found to violate the Nernst heat theorem if the dc conductivity of a dielectric body is included in calculations and in agreement with this theorem otherwise [58–62]. Thus, the theoretical approach consistent with the results of Casimir experiments, in spite of its inconsistency with clearly established facts in other fields of physics, was again found in accordance with the requirements of thermodynamics. The above contradictions have often been called in the literature the Casimir puzzle and the Casimir conundrum (see, e.g., Refs. [63–67]) which still remain unresolved.

From the above reasoning it may be suggested that the Nernst heat theorem plays an important role as a test for different approaches to a description of the dielectric response of matter. The weak point of existing approaches is the use of phenomenological local dielectric permittivities given by the Drude and plasma models. It is the matter of fact that real dielectrics and metals are too complicated systems, so that their response to the electromagnetic field cannot be found exactly on the basis of first principles of thermal quantum field theory. In this regard, much attention is currently attracted to graphene which is a 2D sheet of carbon atoms packed in a hexagonal lattice. The remarkable feature of graphene is that at energies below 1–2 eV it is described by the Dirac model where the speed of light is replaced with the Fermi velocity $v_F \approx c/300$ [68–70]. This opens opportunities for a full description of the nonlocal dielectric properties of graphene in the framework of thermal quantum field theory in the Matsubara formulation. It should be noted also that the Casimir-Polder interaction of different atoms with graphene and graphene-coated substrates attracts much recent attention [71–80]. This raises a question on whether or not the Casimir and Casimir-Polder entropy in graphene systems is consistent with the Nernst heat theorem.

This question can be investigated by describing the dielectric response of graphene in terms of its polarization tensor. The exact expressions for the polarization tensor of graphene with a nonzero energy gap Δ at zero temperature have been found in Ref. [81]. In Ref. [82] they were generalized for the case of nonzero temperature, but only at the pure imaginary Matsubara frequencies. In Ref. [83] another representation for the polarization tensor of graphene was obtained valid over the entire plane of complex frequencies. In Ref. [84] it was generalized to the case of nonzero chemical potential μ. A validity of the Kramers-Kronig relations for the obtained dielectric response has been demonstrated in Ref. [85]. Thus, it was proven that the dielectric response of graphene satisfies the causality condition. Using the results of Ref. [83], it was shown that the Casimir entropy of two parallel sheets of pristine graphene, possessing the zero energy gap and chemical potential, as well as the Casimir-Polder entropy for an atom interacting with a pristine graphene sheet, satisfy the Nernst heat theorem [86,87]. The low-temperature expansion of the Casimir-Polder free energy for an atom interacting with real graphene sheet possessing any values of Δ and μ was considered in Ref. [88], and several main terms under different relationships between Δ and μ have been found. Some of them, however, turned out to be in disagreement with the results of Ref. [89] obtained only in the special case $\Delta > 2\mu$. Thus, the issue on a validity of the Nernst heat theorem for an atom interacting with real graphene sheet remained open.

In this paper, we investigate the analytic behavior of the Casimir-Polder free energy and entropy at low temperature for an atom interacting with real graphene sheet for any relationships between the energy gap Δ and chemical potential μ basing on first principles of thermal quantum field theory in the Matsubara formulation. For this purpose, the thermal correction to the Casimir-Polder energy is presented as a sum of three contributions. The first of them is obtained using the polarization tensor of graphene at zero temperature. In this case the temperature dependence arises only due to a summation over the Matsubara frequencies. The second and third contributions originate from an explicit dependence of the polarization tensor on temperature as a parameter in the Matsubara term with zero frequency and in the sum of terms with all nonzero Matsubara frequencies, respectively. It is shown that for $\Delta > 2\mu$ the Casimir-Polder free energy at sufficiently low temperature behaves as $\sim(k_BT)^5$, where k_B is the Boltzmann constant whereas for $\Delta < 2\mu$ as $\sim(k_BT)^2$. These behaviors are determined by the first contribution to the thermal correction. The conclusion is made that for $\Delta > 2\mu$ and $\Delta < 2\mu$ the Casimir-Polder free energy and entropy for an atom interacting with graphene sheet are in agreement with the Nernst heat theorem. The main terms of the second and third contributions in the thermal correction to the Casimir-Polder energy are also found. According to the obtained results, for $\Delta = 2\mu$ the Casimir-Polder free energy at low temperature is of the order of k_BT and is determined by the third contribution to the thermal correction. The physical meaning of the resulting entropic anomaly is discussed.

The paper is organized as follows. In Sec. II, the Casimir-Polder free energy for an atom interacting with real graphene sheet is conveniently expressed via the polarization tensor. In Sec. III, the low-temperature behavior of the first contribution to the thermal correction arising due to the Matsubara summation is found using the polarization tensor at zero temperature. Section IV considers the second contribution to the thermal correction arising from an explicit temperature dependence of the polarization tensor in the zero-frequency Matsubara term. In Sec. V, the third contribution to the thermal correction is found at low temperature which arises in a similar manner from the sum of all terms with nonzero Matsubara frequencies. In Sec. VI, the reader will find our conclusions and a discussion. Appendices A and B contain some details of the used asymptotic expansions.

II. THE CASIMIR-POLDER FREE ENERGY FOR AN ATOM INTERACTING WITH REAL GRAPHENE SHEET DESCRIBED BY THE POLARIZATION TENSOR

The free energy of an atom spaced at a distance a from real graphene sheet kept at temperature T in thermal equilibrium with the environment has the form following from the Lifshitz theory for an atom interacting with any plate or some planar structure [43]. For our purposes, it is convenient to present this equation in terms of dimensionless Matsubara frequencies $\zeta_l = \xi_l/\omega_c$, where $l = 0, 1, 2, \ldots$, $\xi_l = 2\pi k_BTl/\hbar$ are the standard dimensional Matsubara frequencies, and $\omega_c = c/(2a)$ is the characteristic frequency. We also use the dimensionless integration variable y which is connected with the magnitude of the wave vector projection on the plane of a plate $k_\perp$ by $y = 2a(k_\perp^2 + \xi_l^2/c^2)^{1/2}$. Then the Casimir-Polder free energy is expressed as

$$\mathcal{F}(a,T) = -\frac{k_BT}{8a^3}\sum_{l=0}^{\infty}{}'\alpha_l\int_{\zeta_l}^{\infty}dy e^{-y} \times [(2y^2-\zeta_l^2)r_{\rm TM}(i\zeta_l,y,T) - \zeta_l^2 r_{\rm TE}(i\zeta_l,y,T)], \quad (1)$$

where $\alpha_l \equiv \alpha(i\omega_c\zeta_l)$ is the atomic electric polarizability, the prime on the summation sign divides the term with $l = 0$ by two, and $r_{\rm TM}$, $r_{\rm TE}$ are the reflection coefficients of electromagnetic waves with the transverse magnetic (TM) and transverse electric (TE) polarizations on the plate (planar structure).

For a dielectric plate described by some phenomenological dielectric permittivity, $r_{\rm TM}$ are $r_{\rm TE}$ are the standard Fresnel reflection coefficients. However, for graphene the reflection coefficients are expressed via the polarization tensor of graphene found on the basis of first principles of thermal quantum field theory [81–84]. For us it is convenient to use the dimensionless polarization tensor $\tilde{\Pi}_{mn,l}(y,T,\Delta,\mu) \equiv \tilde{\Pi}_{mn}(i\zeta_l,y,T,\Delta,\mu)$, where m, $n = 0$, 1, 2 are the tensor indices and l is the index of the Matsubara summation defined above. The tensor $\tilde{\Pi}_{mn,l}$ is expressed via the dimensional one by $\tilde{\Pi}_{mn,l} = 2a\Pi_{mn,l}/\hbar$. Then the reflection coefficients on a graphene sheet take the form [81–84]

$$r_{\rm TM}(i\zeta_l,y,T) = \frac{y\tilde{\Pi}_{00,l}(y,T,\Delta,\mu)}{y\tilde{\Pi}_{00,l}(y,T,\Delta,\mu) + 2(y^2-\zeta_l^2)},$$
$$r_{\rm TE}(i\zeta_l,y,T) = -\frac{\tilde{\Pi}_l(y,T,\Delta,\mu)}{\tilde{\Pi}_l(y,T,\Delta,\mu) + 2y(y^2-\zeta_l^2)}. \quad (2)$$

Here, the quantity $\tilde{\Pi}_l(y,T,\Delta,\mu) \equiv \tilde{\Pi}(i\zeta_l,y,T,\Delta,\mu)$ is not a tensor, but the following linear combination of the trace of the polarization tensor $\tilde{\Pi}_m^m(i\zeta_l,y,T,\Delta,\mu)$ and its 00 component $\tilde{\Pi}_{00}(i\zeta_l,y,T,\Delta,\mu)$:

$$\tilde{\Pi}(i\zeta_l,y,T,\Delta,\mu) = (y^2-\zeta_l^2)\tilde{\Pi}_m^m(i\zeta_l,y,T,\Delta,\mu) - y^2\tilde{\Pi}_{00}(i\zeta_l,y,T,\Delta,\mu). \quad (3)$$

(Note that in the literature this combination is usually notated by the same letter as the tensor components which does not create confusion because it does not have the tensor indices.) It was shown [82] that the polarization tensor of graphene is completely determined by its 00 component and by its trace, but in numerous applications it is more convenient [83] to use, in addition to $\tilde{\Pi}_{00,l}$, not the trace itself but the quantity $\tilde{\Pi}_l$ defined in Eq. (3).

For real graphene sheet the quantities $\tilde{\Pi}_{00,l}$ and $\tilde{\Pi}_l$ depend on the energy gap Δ and chemical potential μ. (Thus, the reflection coefficients also depend on Δ and μ, but we do not explicitly indicate this dependence for the sake of brevity.) Note that a nonzero energy gap in the spectrum of electronic excitations arises under the influence of electron-electron interaction, defects of the crystal structure, for graphene deposited on a substrate etc., [70,90,91], whereas the value of the chemical potential is connected with the doping concentration [92]. Explicit expressions for $\tilde{\Pi}_{00,l}$ and $\tilde{\Pi}_l$ can be conveniently presented as the sums of independent and dependent on μ and T parts [80],

$$\begin{aligned}\tilde{\Pi}_{00,l}(y,T,\Delta,\mu) &= \tilde{\Pi}_{00,l}^{(0)}(y,\Delta)+\tilde{\Pi}_{00,l}^{(1)}(y,T,\Delta,\mu),\\ \tilde{\Pi}_{l}(y,T,\Delta,\mu) &= \tilde{\Pi}_{l}^{(0)}(y,\Delta)+\tilde{\Pi}_{l}^{(1)}(y,T,\Delta,\mu).\end{aligned} \tag{4}$$

As the independent on μ and T parts on the right-hand side of Eq. (4) we take the respective quantities from Refs. [80,81]:

$$\begin{aligned}\tilde{\Pi}_{00,l}^{(0)}(y,\Delta) &= \alpha\frac{y^2-\zeta_l^2}{p_l}\Psi\left(\frac{D}{p_l}\right),\\ \tilde{\Pi}_{l}^{(0)}(y,\Delta) &= \alpha(y^2-\zeta_l^2)p_l\Psi\left(\frac{D}{p_l}\right).\end{aligned} \tag{5}$$

Here, $D \equiv \Delta/(\hbar\omega_c)$, the function $\Psi(x)$ is defined as

$$\Psi(x) = 2[x+(1-x^2)\arctan(x^{-1})], \tag{6}$$

$\alpha = e^2/(\hbar c)$ [in SI units $e^2/(4\pi\epsilon_0\hbar c)$ where ϵ_0 is the permittivity of the vacuum] and $\tilde{v}_F = v_F/c \approx 1/300$ are the fine structure constant and the Fermi velocity normalized to the speed of light, and

$$p_l = [\tilde{v}_F^2y^2+(1-\tilde{v}_F^2)\zeta_l^2]^{1/2}. \tag{7}$$

The μ-dependent parts on the right-hand side of Eq. (4) are more complicated. They are given by Eqs. (13) and (14) in Ref. [80] where it is convenient to replace the integration variable u with $t = \hbar c p_l u/(2a\Delta)$:

$$\begin{aligned}\tilde{\Pi}_{00,l}^{(1)}(y,T,\Delta,\mu) &= \frac{4\alpha D}{\tilde{v}_F^2}\int_1^\infty dt w(t,T,\Delta,\mu)X_{00,l}(t,y,D),\\ \tilde{\Pi}_{l}^{(1)}(y,T,\Delta,\mu) &= -\frac{4\alpha D}{\tilde{v}_F^2}\int_1^\infty dt w(t,T,\Delta,\mu)X_{l}(t,y,D),\end{aligned} \tag{8}$$

where w is defined as

$$w(t,T,\Delta,\mu) = \left(e^{\frac{t\Delta+2\mu}{2k_BT}}+1\right)^{-1}+\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1} \tag{9}$$

and the quantities $X_{00,l}$ and X_l are given by

$$\begin{aligned}X_{00,l}(t,y,D) &= 1-\mathrm{Re}\frac{p_l^2-D^2t^2+2i\zeta_lDt}{[p_l^4-p_l^2D^2t^2+\tilde{v}_F^2(y^2-\zeta_l^2)D^2+2i\zeta_lp_l^2Dt]^{1/2}},\\ X_l(t,y,D) &= \zeta_l^2-\mathrm{Re}\frac{\zeta_l^2p_l^2-p_l^2D^2t^2+\tilde{v}_F^2(y^2-\zeta_l^2)D^2+2i\zeta_lp_l^2Dt}{[p_l^4-p_l^2D^2t^2+\tilde{v}_F^2(y^2-\zeta_l^2)D^2+2i\zeta_lp_l^2Dt]^{1/2}}.\end{aligned} \tag{10}$$

As noted in Sec. I, we are interested to investigate the thermal correction to the Casimir-Polder energy as a function of temperature. For this purpose the Casimir-Polder free energy is presented in the form

$$\mathcal{F}(a,T) = E(a)+\delta_T\mathcal{F}(a,T), \tag{11}$$

where the Casimir-Polder energy is given by

$$\begin{aligned}E(a) = -\frac{\hbar c}{32\pi a^4}&\int_0^\infty d\zeta\alpha(i\omega_c\zeta)\int_\zeta^\infty dye^{-y}\\ &\times[(2y^2-\zeta^2)r_{\mathrm{TM}}(i\zeta,y,0)-\zeta^2r_{\mathrm{TE}}(i\zeta,y,0],\end{aligned} \tag{12}$$

and the thermal correction vanishes with vanishing temperature

$$\lim_{T\to 0}\delta_T\mathcal{F}(a,T) = 0. \tag{13}$$

The reflection coefficients in Eq. (12) are given by Eq. (2) taken at $T = 0$. They are expressed via the polarization tensor of graphene calculated at zero temperature and contain a continuous parameter ζ in place of the discrete Matsubara frequencies ζ_l.

An important point is that in the limiting case of zero chemical potential, $\mu \to 0$, the quantities $\tilde{\Pi}_{00,l}^{(0)}$ and $\tilde{\Pi}_{l}^{(0)}$ defined in Eqs. (4) and (5) just have the meaning of the 00 component of the polarization tensor at zero temperature and the combination of its components defined in Eq. (3):

$$\begin{aligned}\tilde{\Pi}_{00,l}^{(0)}(y,\Delta) &= \tilde{\Pi}_{00,l}(y,0,\Delta,0),\\ \tilde{\Pi}_{l}^{(0)}(y,\Delta) &= \tilde{\Pi}_{l}(y,0,\Delta,0).\end{aligned} \tag{14}$$

In this case the quantities $\tilde{\Pi}_{00,l}^{(1)}$ and $\tilde{\Pi}_{l}^{(1)}$ have the meaning of the thermal corrections to the zero-temperature polarization tensor:

$$\begin{aligned}\tilde{\Pi}_{00,l}^{(1)}(y,T,\Delta,0) &= \delta_T\tilde{\Pi}_{00,l}(y,T,\Delta,0),\\ \tilde{\Pi}_{l}^{(1)}(y,T,\Delta,0) &= \delta_T\tilde{\Pi}_{l}(y,T,\Delta,0),\end{aligned} \tag{15}$$

which goes to zero with vanishing T.

According to the results of Ref. [80], a similar situation holds for $\mu \neq 0$ satisfying the condition $\Delta > 2\mu$. Under this condition the polarization tensor at zero temperature does not depend on μ, so that, once again, we have

$$\begin{aligned}\tilde{\Pi}_{00,l}^{(0)}(y,\Delta) &= \tilde{\Pi}_{00,l}(y,0,\Delta,\mu),\\ \tilde{\Pi}_{l}^{(0)}(y,\Delta) &= \tilde{\Pi}_{l}(y,0,\Delta,\mu),\end{aligned} \tag{16}$$

and

$$\begin{aligned}\tilde{\Pi}_{00,l}^{(1)}(y,T,\Delta,\mu) &= \delta_T\tilde{\Pi}_{00,l}(y,T,\Delta,\mu),\\ \tilde{\Pi}_{l}^{(1)}(y,T,\Delta,\mu) &= \delta_T\tilde{\Pi}_{l}(y,T,\Delta,\mu),\end{aligned} \tag{17}$$

where the quantities in Eq. (17) go to zero when T goes to zero.

Another situation takes place for $\mu \neq 0$ satisfying the condition $\Delta < 2\mu$. In this case the quantities $\tilde{\Pi}_{00,l}^{(0)}$ and $\tilde{\Pi}_{l}^{(0)}$ are not equal to the 00 component of the polarization tensor at zero temperature and to the combination of its components defined in Eq. (3). In fact under the condition $\Delta < 2\mu$ the polarization tensor at $T = 0$ depends on μ. The precise expressions for the quantities $\tilde{\Pi}_{00,l}(y,0,\Delta,\mu)$ and $\tilde{\Pi}_{l}(y,0,\Delta,\mu)$ in this case have been obtained in Eqs. (21) and (24) of Ref. [93] by direct calculation using Eqs. (4)–(10). In terms of the dimensionless variables used above they are given by

$$\begin{aligned}\tilde{\Pi}_{00,l}(y,0,\Delta,\mu) &= \frac{8\alpha\mu}{\tilde{v}_F^2\hbar\omega_c} - \frac{2\alpha(y^2-\zeta_l^2)}{p_l^3}\left\{(p_l^2+D^2)\,\mathrm{Im}\left(z_l\sqrt{1+z_l^2}\right) + (p_l^2-D^2)\left[\mathrm{Im}\ln\left(z_l+\sqrt{1+z_l^2}\right) - \frac{\pi}{2}\right]\right\},\\ \tilde{\Pi}_{l}(y,0,\Delta,\mu) &= -\frac{8\alpha\mu\zeta_l^2}{\tilde{v}_F^2\hbar\omega_c} + \frac{2\alpha(y^2-\zeta_l^2)}{p_l}\left\{(p_l^2+D^2)\,\mathrm{Im}\left(z_l\sqrt{1+z_l^2}\right) - (p_l^2-D^2)\left[\mathrm{Im}\ln\left(z_l+\sqrt{1+z_l^2}\right) - \frac{\pi}{2}\right]\right\},\end{aligned} \tag{18}$$

where

$$z_l \equiv z_l(y,\Delta,\mu) = \frac{p_l}{\tilde{v}_F\sqrt{p_l^2+D^2}\sqrt{y^2-\zeta_l^2}}\left(\zeta_l + \mathrm{i}\frac{2\mu}{\hbar\omega_c}\right). \tag{19}$$

It is easily seen that for $\mu = \Delta = 0$ these equations reduce to the result given by Eq. (5) with $\Delta = 0$.

Now we are in a position to present the reflection coefficients (2) in the form

$$r_{\mathrm{TM(TE)}}(\mathrm{i}\zeta_l,y,T) = r_{\mathrm{TM(TE)}}(\mathrm{i}\zeta_l,y,0) + \delta_T r_{\mathrm{TM(TE)}}(\mathrm{i}\zeta_l,y,T), \tag{20}$$

where the first contributions on the right-hand side are determined by the polarization tensor at $T = 0$:

$$\begin{aligned}r_{\mathrm{TM}}(\mathrm{i}\zeta_l,y,0) &= \frac{y\tilde{\Pi}_{00,l}(y,0,\Delta,\mu)}{y\tilde{\Pi}_{00,l}(y,0,\Delta,\mu) + 2(y^2-\zeta_l^2)},\\ r_{\mathrm{TE}}(\mathrm{i}\zeta_l,y,0) &= -\frac{\tilde{\Pi}_{l}(y,0,\Delta,\mu)}{\tilde{\Pi}_{l}(y,0,\Delta,\mu) + 2y(y^2-\zeta_l^2)},\end{aligned} \tag{21}$$

whereas the second contribution has the meaning of the thermal correction and goes to zero with vanishing T. This equation, however, is valid in both cases $\Delta > 2\mu$ [here, in accordance to Eq. (16), the polarization tensor at $T = 0$ is presented in Eq. (5)] and $\Delta < 2\mu$ [here it is given by Eq. (18)]. As to the case $\Delta = 2\mu$, it is discussed in the next sections, as well as the explicit approximate expressions for thermal corrections to the reflection coefficients on the right-hand side of Eq. (20).

Using Eq. (11), we present the thermal correction to the Casimir-Polder energy as

$$\delta_T\mathcal{F}(a,T) = \mathcal{F}(a,T) - E(a). \tag{22}$$

Now we substitute Eq. (20) in the expression (1) for the Casimir-Polder free energy and identically present the thermal correction $\delta_T\mathcal{F}$ as a sum of three contributions:

$$\delta_T\mathcal{F}(a,T) = \delta_T^{\mathrm{impl}}\mathcal{F}(a,T) + \delta_{T,l=0}^{\mathrm{expl}}\mathcal{F}(a,T) + \delta_{T,l\geq 1}^{\mathrm{expl}}\mathcal{F}(a,T). \tag{23}$$

Here, the following notations are introduced:

$$\begin{aligned}\delta_T^{\mathrm{impl}}\mathcal{F}(a,T) \equiv -\frac{k_BT}{8a^3}{\sum_{l=0}^{\infty}}{}'\alpha_l\int_{\zeta_l}^{\infty}dy e^{-y}&\\ \times[(2y^2-\zeta_l^2)r_{\mathrm{TM}}(\mathrm{i}\zeta_l,y,0)&\\ -\zeta_l^2 r_{\mathrm{TE}}(\mathrm{i}\zeta_l,y,0)] - E(a),&\end{aligned} \tag{24}$$

where $E(a)$ is defined in Eq. (12), and

$$\begin{aligned}&\delta_{T,l=0}^{\mathrm{expl}}\mathcal{F}(a,T) + \delta_{T,l\geq 1}^{\mathrm{expl}}\mathcal{F}(a,T)\\ &\quad\equiv -\frac{k_BT}{8a^3}{\sum_{l=0}^{\infty}}{}'\alpha_l\int_{\zeta_l}^{\infty}dy e^{-y}[(2y^2-\zeta_l^2)\delta_T r_{\mathrm{TM}}(\mathrm{i}\zeta_l,y,T)\\ &\quad - \zeta_l^2\delta_T r_{\mathrm{TE}}(\mathrm{i}\zeta_l,y,T)],\end{aligned} \tag{25}$$

where $\delta_{T,l=0}^{\mathrm{expl}}\mathcal{F}$ and $\delta_{T,l\geq 1}^{\mathrm{expl}}\mathcal{F}$ are equal to the term with $l = 0$ and to the sum of the terms with $l \geq 1$, respectively, in Eq. (25).

From Eq. (24) it is seen that the contribution to the thermal correction $\delta_T^{\rm impl}\mathcal{F}$ contains only the reflection coefficients at zero temperature. Thus, its temperature dependence is completely determined by a summation over the Matsubara frequencies. For this reason, it is called “implicit.” As to the contributions $\delta_{T,l=0}^{\rm expl}\mathcal{F}$ and $\delta_{T,l\geq 1}^{\rm expl}\mathcal{F}$ to the thermal correction, defined in Eq. (25), they depend on the thermal corrections to the reflection coefficients which vanish if the polarization tensor does not depend on temperature as a parameter. Because of this, the contributions $\delta_{T,l=0}^{\rm expl}\mathcal{F}$ and $\delta_{T,l\geq 1}^{\rm expl}\mathcal{F}$ are called “explicit.” In fact the quantity in Eq. (25) could be considered as one explicit contribution to the thermal correction. However, the asymptotic behaviors of $\delta_{T,l=0}^{\rm expl}\mathcal{F}$ and $\delta_{T,l\geq 1}^{\rm expl}\mathcal{F}$ with vanishing T are not similar (see Secs. IV and V), and this fact warrants a division of this contribution into two parts.

In the next sections, the low-temperature behaviors of the thermal corrections $\delta_T^{\rm impl}\mathcal{F}$, $\delta_{T,l=0}^{\rm expl}\mathcal{F}$ and $\delta_{T,l\geq 1}^{\rm expl}\mathcal{F}$ are investigated one after another.

III. THERMAL CORRECTION TO THE CASIMIR-POLDER ENERGY DUE TO MATSUBARA SUMMATION USING THE ZERO-TEMPERATURE REFLECTION COEFFICIENTS

In this section, we find the behavior of the first contribution to the thermal correction, $\delta_T^{\rm impl}\mathcal{F}$, at low temperature under different relationships between the energy gap and chemical potential. As defined in Eq. (24), $\delta_T^{\rm impl}\mathcal{F}$ is given by the difference of the sum over the discrete Matsubara frequencies with the reflection coefficients $r_{\rm TM(TE)}({\rm i}\zeta_l,y,0)$, and the integral with respect to continuous imaginary frequency containing the reflection coefficients $r_{\rm TM(TE)}({\rm i}\zeta,y,0)$. Using the Abel-Plana formula, this difference can be written in the form [43,87]

$$\delta_T^{\rm impl}\mathcal{F}(a,T)=-{\rm i}\frac{\alpha_0k_BT}{8a^3}\int_0^\infty dt\frac{\Phi({\rm i}t\tau)-\Phi(-{\rm i}t\tau)}{e^{2\pi t}-1},\qquad(26)$$

where $\Phi(x)=\Phi_1(x)+\Phi_2(x)$,

$$\begin{aligned}\Phi_1(x)&=2\int_x^\infty dy y^2e^{-y}r_{\rm TM}({\rm i}x,y,0),\\ \Phi_2(x)&=-x^2\int_x^\infty dy e^{-y}[r_{\rm TM}({\rm i}x,y,0)+r_{\rm TE}({\rm i}x,y,0)]\end{aligned}\qquad(27)$$

and the dimensionless temperature parameter is defined as $\tau=4\pi ak_BT/(\hbar c)=2\pi k_BT/(\hbar\omega_c)$.

In Eq. (26), we have preserved only the static atomic polarizability $\alpha_0=\alpha(0)$ in the expansion of $\alpha({\rm i}t\tau)=\alpha({\rm i}x)$ in the powers of x. This is because we are looking for the main term in the expansion of the Casimir-Polder free energy $\mathcal{F}$ at low T ($\tau\ll 1$). Note also that care must be exercised when expanding the functions Φ_1 and Φ_2 in the powers of x. It may happen that an expansion of the reflection coefficients in the powers of x with subsequent integration leads to incorrect results because common powers of x arise from different expansion orders of the reflection coefficients (see below).

We begin with the case of a slightly doped graphene $\Delta>2\mu$. In this case the polarization tensor at zero temperature does not depend on μ [see Eq. (16)] and is given by Eq. (5). The reflection coefficients entering the thermal correction $\delta_T^{\rm impl}\mathcal{F}(a,T)$ are given by Eq. (21). For the function Φ_1, defined in Eq. (27), it is not productive to expand the reflection coefficient $r_{\rm TM}$ in powers of x with subsequent integration as noted above. Instead, an expansion of Φ_1 in the Taylor series in powers of x using Eqs. (5) and (21) results in $\Phi_1'(0)=\Phi_1^{(3)}(0)=\Phi_1^{(5)}(0)=0$. Then we conclude that the leading contribution of Φ_1 to $\delta_T^{\rm impl}\mathcal{F}(a,T)$ is of higher order than T^6 because the even powers in x do not contribute to Eq. (26).

An expansion of the function Φ_2 defined in Eq. (27) in powers of x can be found by expanding the sum of the reflection coefficients $r_{\rm TM}$ and $r_{\rm TE}$ in powers of x with subsequent integration with respect to y. This is done under an assumption $D>1$ which is valid at sufficiently large separations $a>1$ μm. Taking into account that the main contributions to the integrals in Eq. (27) are given by $y\sim 1$ and that $\zeta_l=\tau l$, at low temperature the quantity p_l defined in Eq. (7) satisfies the inequality $p_l\ll 1$, so that $D/p_l\gg 1$. Then the main contribution to the function Ψ in Eqs. (5) and (6) is given by

$$\Psi\left(\frac{D}{p_l}\right)\approx\frac{8}{3}\frac{p_l}{D}.\qquad(28)$$

With account of this equation one obtains [89]

$$\Phi_2(x)=\frac{\hbar c\alpha(1+\tilde{v}_F^2)}{3\tilde{v}_F^2a\Delta}x^4{\rm Ei}(-x)+Cx^4+O(x^5),\qquad(29)$$

where ${\rm Ei}(z)$ is the exponential integral and C is a constant which does not contribute to Eq. (26).

Substituting Eq. (29) in Eq. (26), one finds [89]

$$\delta_T^{\rm impl}\mathcal{F}(a,T)=-\frac{\alpha_0(k_BT)^5}{(\hbar c)^3\Delta}\frac{8\alpha(1+\tilde{v}_F^2)}{\tilde{v}_F^2}.\qquad(30)$$

Thus, under a condition $\Delta>2\mu$ the thermal correction $\delta_T^{\rm impl}\mathcal{F}$ vanishes with temperature faster than for a pristine graphene where it is of the order of $(k_BT)^4$ [87].

We are coming now to the case of $\Delta<2\mu$. In this case the thermal correction $\delta_T^{\rm impl}\mathcal{F}$ is again given by the difference of the sum Eq. (1) with the zero-temperature reflection coefficients $r_{\rm TM(TE)}({\rm i}\zeta_l,y,0)$ and the integral (12) resulting in Eq. (26). It is convenient, however, to present the function $\Phi(x)$ in an equivalent form $\Phi(x) = \chi_1(x) + \chi_2(x)$, where

$$\chi_1(x) = \int_x^\infty dy e^{-y}(2y^2 - x^2) r_{\mathrm{TM}}(\mathrm{i}x, y, 0),$$
$$\chi_2(x) = -x^2 \int_x^\infty dy e^{-y} r_{\mathrm{TE}}(\mathrm{i}x, y, 0). \tag{31}$$

The reflection coefficients are again given by Eq. (21), but the polarization tensor is now presented in Eqs. (18) and (19) where the discrete Matsubara frequencies $\zeta_l = \tau l$ are replaced with x. Then the polarization tensor in Eq. (21) is replaced with $\tilde{\Pi}_{00}(x, y, 0, \Delta, \mu)$. The low-temperature expansion of the quantity $\chi_1(x)$ can be performed in the same way as of $\Phi_1(x)$, i.e., by expanding $\chi_1(x)$ in the Taylor series in powers of x. Using Eqs. (31) and (21), one obtains

$$\chi_1'(0) = 2\int_0^\infty dy e^{-y} y^2 \frac{\partial}{\partial x} \frac{y\tilde{\Pi}_{00}(x,y,0,\Delta,\mu)}{y\tilde{\Pi}_{00}(x,y,0,\Delta,\mu) + 2(y^2 - x^2)}\bigg|_{x=0}$$
$$= 4\int_0^\infty dy e^{-y} y^3 \frac{\frac{\partial}{\partial x}\tilde{\Pi}_{00}(x,y,0,\Delta,\mu)|_{x=0}}{[\tilde{\Pi}_{00}(0,y,0,\Delta,\mu) + 2y]^2}. \tag{32}$$

In what follows we use the condition

$$\sqrt{4\mu^2 - \Delta^2} > \hbar\omega_c, \tag{33}$$

which is valid at sufficiently large separations. Then from the first formula in Eq. (18) we have

$$\tilde{\Pi}_{00}(0, y, 0, \Delta, \mu) = \frac{8\alpha}{\tilde{v}_F^2} \frac{\mu}{\hbar\omega_c} \equiv Q_0. \tag{34}$$

By calculating the derivative of the first formula in Eq. (18) at $x = 0$, we obtain

$$\frac{\partial}{\partial x}\tilde{\Pi}_{00}(x,y,0,\Delta,\mu)\bigg|_{x=0} = -\frac{4\alpha}{\tilde{v}_F^3 y} \frac{4\mu^2 - (\hbar\omega_c\tilde{v}_F y)^2}{\sqrt{4\mu^2 - (\hbar\omega_c\tilde{v}_F y)^2 - \Delta^2}}. \tag{35}$$

Taking into account the condition (33), the inequality $\tilde{v}_F \ll 1$ and the fact that the main contribution to Eq. (32) is given by $y \sim 1$, Eq. (35) can be simplified to

$$\frac{\partial}{\partial x}\tilde{\Pi}_{00}(x, y, 0, \Delta, \mu)\bigg|_{x=0} = -\frac{16\alpha}{\tilde{v}_F^3 y} \frac{\mu^2}{\hbar\omega_c\sqrt{4\mu^2 - \Delta^2}}. \tag{36}$$

Substituting Eqs. (34) and (36) in Eq. (32), one finds

$$\chi_1'(0) = -\frac{16\alpha\mu^2}{\tilde{v}_F^3\hbar\omega_c\sqrt{4\mu^2 - \Delta^2}} \int_0^\infty dy e^{-y} \frac{4y^2}{(2y + Q_0)^2}$$
$$= -\frac{16\alpha\mu^2}{\tilde{v}_F^3\hbar\omega_c\sqrt{4\mu^2 - \Delta^2}} \left[\frac{2 + Q_0}{2} + \frac{Q_0(Q_0 + 4)}{4} e^{Q_0/2}\mathrm{Ei}\left(-\frac{Q_0}{2}\right)\right]. \tag{37}$$

Now we have the desired result

$$\chi_1(x) = \chi_1(0) + \chi_1'(0)x + O(x^2), \tag{38}$$

where $\chi_1(0)$ does not contribute to Eq. (26) and the value of the first derivative at $x = 0$ is presented in Eq. (37). From Eq. (31) it is easily seen that $\chi_2(0) = \chi_2'(0) = 0$ and similar expansion for the function $\chi_2(x)$ takes the form

$$\chi_2(x) = Cx^2 + O(x^3), \tag{39}$$

where C is a constant which does not contribute to Eq. (26). Thus, from Eq. (38)

$$\Phi(\mathrm{i}\tau t) - \Phi(-\mathrm{i}\tau t) = 2\mathrm{i}\chi_1'(0)\tau t \tag{40}$$

and, after substitution to Eq. (26) with account of Eq. (37), one obtains

$$\delta_T^{\mathrm{impl}}\mathcal{F}(a,T) = -\frac{\alpha_0\mu^2(k_BT)^2}{(\hbar c)^2 a\sqrt{4\mu^2 - \Delta^2}} \frac{16\alpha}{\tilde{v}_F^3}$$
$$\times \left[2 + Q_0 + \frac{Q_0(Q_0 + 4)}{2} e^{Q_0/2}\mathrm{Ei}\left(-\frac{Q_0}{2}\right)\right]. \tag{41}$$

It is seen that in the case $\Delta < 2\mu$ the behavior of the thermal correction $\delta_T^{\mathrm{impl}}\mathcal{F}$ at low temperature is different from the case of graphene with $\Delta > 2\mu$ [see Eq. (30)] and from the case of pristine graphene.

Now we consider the low-temperature behavior of $\delta_T^{\mathrm{impl}}\mathcal{F}$ for the case $\Delta = 2\mu$. This case cannot be considered by the limiting transition $\Delta \to 2\mu$ from our result (41) obtained for $\Delta < 2\mu$ because it was derived under the condition (33).

Below we show that in the case $\Delta = 2\mu$ the low-temperature behavior of $\delta_T^{\mathrm{impl}}\mathcal{F}$ is again given by Eq. (30) derived in the case $\Delta > 2\mu$. We start from the polarization

TABLE I. Up to an order of magnitude asymptotic behaviors at low temperature for the magnitudes of three different terms in the thermal correction to the Casimir-Polder energy (columns 2–4), thermal correction itself (column 5), and the Casimir-Polder entropy (column 6) for different relationships between the energy gap and the chemical potential (column 1). See the text for further discussion.

Δ	$r_\alpha(\mathrm{i}\zeta_l, y, 0)$	$\delta_T r_\alpha(\mathrm{i}\zeta_l, y, T)$		$r_\alpha(\mathrm{i}\zeta_l, y, T)$	
versus	$l \geq 0$	$l = 0$	$l \geq 1$	$l \geq 0$	
μ	$\vert\delta_T^{\mathrm{impl}}\mathcal{F}(a,T)\vert$	$\vert\delta_{T,l=0}^{\mathrm{expl}}\mathcal{F}(a,T)\vert$	$\vert\delta_{T,l\geq 1}^{\mathrm{expl}}\mathcal{F}(a,T)\vert$	$\vert\delta_T\mathcal{F}(a,T)\vert$	$S(a,T)$
$\Delta > 2\mu$	$\frac{\alpha_0(k_BT)^5}{(\hbar c)^3\Delta}$	$\frac{\alpha_0(k_BT)^2}{\hbar c a^2}e^{-\frac{\Delta-2\mu}{2k_BT}}$	$\frac{\alpha_0 k_BT}{a^3}e^{-\frac{\Delta-2\mu}{2k_BT}}$	$\frac{\alpha_0(k_BT)^5}{(\hbar c)^3\Delta}$	$\frac{\alpha_0 k_B(k_BT)^4}{(\hbar c)^3\Delta}$
$\Delta < 2\mu$	$\frac{\alpha_0\mu^2(k_BT)^2}{(\hbar c)^2 a(4\mu^2-\Delta^2)^{1/2}}$	$\frac{\alpha_0 k_BT}{a^3}e^{-\frac{2\mu-\Delta}{2k_BT}}$	$\frac{\alpha_0\hbar c}{a^4}e^{-\frac{2\mu-\Delta}{2k_BT}}$	$\frac{\alpha_0\mu^2(k_BT)^2}{(\hbar c)^2 a(4\mu^2-\Delta^2)^{1/2}}$	$\frac{\alpha_0\mu^2 k_B^2T}{(\hbar c)^2 a(4\mu^2-\Delta^2)^{1/2}}$
$\Delta = 2\mu$	$\frac{\alpha_0(k_BT)^5}{(\hbar c)^3\Delta}$	$\frac{\alpha_0(k_BT)^2}{\hbar c a^2}$	$\frac{\alpha_0 k_BT}{a^3}$	$\frac{\alpha_0 k_BT}{a^3}$	$\frac{\alpha_0 k_B}{a^3}$

tensor at zero temperature (5) where $\zeta_l = \tau l$ is replaced with x. To be specific, we consider

$$\tilde{\Pi}_{00}^{(0)}(x, y, \Delta) = \alpha\frac{y^2 - x^2}{p(x)}\Psi\left(\frac{D}{p(x)}\right), \tag{42}$$

where Ψ is defined in Eq. (6) and $p(x) = [\tilde{v}_F^2 y^2 + (1 - \tilde{v}_F^2)x^2]^{1/2}$. Under the condition $D > 1$, we consider the value of $\tilde{\Pi}_{00}^{(0)}$ at zero x:

$$\tilde{\Pi}_{00}^{(0)}(0, y, \Delta) = \frac{\alpha y}{\tilde{v}_F}\Psi\left(\frac{D}{\tilde{v}_F y}\right). \tag{43}$$

Expanding this quantity in powers of the small parameter $\tilde{v}_F y/D$, one arrives at

$$\tilde{\Pi}_{00}^{(0)}(0, y, \Delta) = \frac{8\alpha y}{\tilde{v}_F}\sum_{k=0}^{\infty}(-1)^k\frac{k+1}{(2k+1)(2k+3)}\left(\frac{\tilde{v}_F y}{D}\right)^{2k+1}. \tag{44}$$

This equation is also valid at $\Delta = 2\mu$. To make sure that this is the case, we consider the first formula in Eq. (18) expressing the zero-temperature polarization tensor in the case $\Delta < 2\mu$, replace there ζ_l with x, put $\mu = \Delta/2$, $x = 0$ and obtain

$$\begin{aligned}&\tilde{\Pi}_{00}(0, y, 0, \Delta, \Delta/2)\\ &\quad= \frac{4\alpha D}{\tilde{v}_F^2} - \frac{2\alpha}{\tilde{v}_F^3 y}\left\{\tilde{v}_F y D + (\tilde{v}_F^2 y^2 - D^2)\right.\\ &\qquad\left.\times\left[\mathrm{Im}\ln(\mathrm{i}D + \tilde{v}_F y) - \frac{\pi}{2}\right]\right\}.\end{aligned} \tag{45}$$

Expanding this equation in powers of $\tilde{v}_F y/D$, one again obtains the right-hand side of Eq. (44) with a conclusion that

$$\tilde{\Pi}_{00}^{(0)}(0, y, \Delta) = \tilde{\Pi}_{00}(0, y, 0, \Delta, \Delta/2). \tag{46}$$

In a similar way, it is easy to show that

$$\tilde{\Pi}^{(0)}(0, y, \Delta) = \tilde{\Pi}(0, y, 0, \Delta, \Delta/2) \tag{47}$$

and also

$$\left.\frac{\partial\tilde{\Pi}_{00}^{(0)}}{\partial x}\right|_{x=0} = \left.\frac{\partial\tilde{\Pi}_{00}}{\partial x}\right|_{x=0} = 0, \quad \left.\frac{\partial\tilde{\Pi}^{(0)}}{\partial x}\right|_{x=0} = \left.\frac{\partial\tilde{\Pi}}{\partial x}\right|_{x=0} = 0. \tag{48}$$

We conclude that the polarization tensor at zero temperature (5) and (18) is continuous at the point $\Delta = 2\mu$, and the thermal correction $\delta_T^{\mathrm{impl}}\mathcal{F}$ at this point is really given by Eq. (30).

For a more lively presentation of the obtained results, we include them in Table I as new information becomes available. The first column in this Table specifies the relationship between the values of Δ and 2μ. Columns 2, 3, and 4 contain up to an order of magnitude asymptotic expressions at low T for the contributions to the thermal correction, $\delta_T^{\mathrm{impl}}\mathcal{F}$, $\delta_{T,l=0}^{\mathrm{expl}}\mathcal{F}$, and $\delta_{T,l\geq 1}^{\mathrm{expl}}\mathcal{F}$, respectively, and indicate the reflection coefficients from which they are obtained. Columns 5 and 6 demonstrate the resulting behaviors of the thermal correction to the Casimir-Polder energy and entropy, respectively, at low temperature. At the moment column 2 includes the results found above in Eqs. (30), (40) and again (30).

IV. THE ROLE OF EXPLICIT TEMPERATURE DEPENDENCE OF REFLECTION COEFFICIENTS: ZERO-FREQUENCY CONTRIBUTION

In this section we consider the low-temperature behavior of the second contribution $\delta_{T,l=0}^{\mathrm{expl}}\mathcal{F}$ to the thermal correction defined by the term of Eq. (25) with $l = 0$. It is given by

$$\delta_{T,l=0}^{\rm expl}\mathcal{F}(a,T)=-\frac{\alpha_0 k_BT}{8a^3}\int_0^\infty dye^{-y}y^2\delta_T r_{\rm TM}(0,y,T). \quad (49)$$

To find $\delta_T r_{\rm TM}$, we substitute the representation for the polarization tensor

$$\tilde\Pi_{00,l}(y,T,\Delta,\mu)=\tilde\Pi_{00,l}(y,0,\Delta,\mu)+\delta_T\tilde\Pi_{00,l}(y,T,\Delta,\mu) \quad (50)$$

in the first formula in Eq. (2) and expand the obtained expression up to the first power in small parameter

$$\frac{\delta_T\tilde\Pi_{00,l}(y,T,\Delta,\mu)}{\tilde\Pi_{00,l}(y,0,\Delta,\mu)}. \quad (51)$$

The result is

$$\delta_T r_{\rm TM}({\rm i}\zeta_l,y,T)=\frac{2y(y^2-\zeta_l^2)\delta_T\tilde\Pi_{00,l}(y,T,\Delta,\mu)}{[y\tilde\Pi_{00,l}(y,0,\Delta,\mu)+2(y^2-\zeta_l^2)]^2}. \quad (52)$$

In this section we use Eq. (52) at $l=0$, but in Sec. V below it is used at all $l\geq 1$.

We start with the case $\Delta>2\mu$ where, according to Eq. (17), $\delta_T\tilde\Pi_{00,0}=\tilde\Pi_{00,0}^{(1)}$. The latter quantity is contained in Eqs. (8)–(10) taken at $l=0$. We restrict ourselves by only the second contribution to the right-hand side of Eq. (9) (below it is shown that the first one leads to an additional exponentially small factor in the result). Thus, the thermal correction to the polarization tensor has the form

$$\begin{aligned}\delta_T\tilde\Pi_{00,0}(y,T,\Delta,\mu)&\\ =\frac{4\alpha D}{\tilde v_F^2}\int_1^\infty dt\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1}&\\ \times\left\{1-{\rm Re}\frac{\tilde v_F^2y^2-D^2t^2}{\tilde v_F y[\tilde v_F^2y^2-D^2(t^2-1)]^{1/2}}\right\}.&\end{aligned} \quad (53)$$

The integral of the first term on the right-hand side of this equation is given by

$$\begin{aligned}\frac{4\alpha D}{\tilde v_F^2}\int_1^\infty dt\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1}&=\frac{8\alpha}{\tilde v_F^2}\frac{k_BT}{\hbar\omega_c}\ln\left(1+e^{-\frac{\Delta-2\mu}{2k_BT}}\right)\\ &\approx\frac{8\alpha}{\tilde v_F^2}\frac{k_BT}{\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}\end{aligned} \quad (54)$$

at $k_BT\ll\Delta-2\mu$.

As shown in Appendix A, for the integral of the second term on the right-hand side of Eq. (53) one has

$$\begin{aligned}&\frac{4\alpha D}{y\tilde v_F^3}\int_1^{f(y)} dt\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1}\frac{D^2t^2-\tilde v_F^2y^2}{[\tilde v_F^2y^2-D^2(t^2-1)]^{1/2}}\\ &<\frac{4\alpha}{\tilde v_F^2}\sqrt{D^2+\tilde v_F^2y^2}\,e^{-\frac{\Delta-2\mu}{2k_BT}}e^{-\frac{(\hbar\omega_c\tilde v_F y)^2}{4k_BT\Delta}},\end{aligned} \quad (55)$$

where

$$f(y)=\sqrt{1+\frac{\tilde v_F^2y^2}{D^2}}. \quad (56)$$

The quantity in Eq. (55) contains an additional factor exponentially small at $T\to 0$, as compared to Eq. (54), and, thus, can be neglected. As a result, we have

$$\delta_T\tilde\Pi_{00,0}(y,T,\Delta,\mu)=\frac{8\alpha}{\tilde v_F^2}\frac{k_BT}{\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}. \quad (57)$$

Note that the first contribution on the right-hand side of Eq. (9) omitted above would lead to an additional exponentially small factor of the order of $e^{-2\mu/(k_BT)}$.

From Eqs. (5) and (28) one also obtains

$$\tilde\Pi_{00,0}(y,0,\Delta,\mu)=\frac{8}{3}\frac{\alpha\hbar\omega_c}{\Delta}y^2. \quad (58)$$

Substituting Eqs. (57) and (58) in Eq. (52) taken at $l=0$, we find

$$\delta_T r_{\rm TM}(0,y,T)=\frac{4\alpha}{\tilde v_F^2}\frac{k_BT}{\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}\frac{1}{y(1+qy)^2}, \quad (59)$$

where $q=4\alpha\hbar\omega_c/(3\Delta)$.

Substituting this equation in Eq. (49) and calculating the integral, one obtains

$$\begin{aligned}\delta_{T,l=0}^{\rm expl}\mathcal{F}(a,T)&=-\alpha_0\frac{\alpha(k_BT)^2}{a^2\tilde v_F^2\hbar c}e^{-\frac{\Delta-2\mu}{2k_BT}}\int_0^\infty dye^{-y}\frac{y}{(1+qy)^2}\\ &=\alpha_0\frac{\alpha(k_BT)^2}{a^2\tilde v_F^2\hbar c}e^{-\frac{\Delta-2\mu}{2k_BT}}\\ &\quad\times\frac{1}{q^2}\left[1+\left(1+\frac{1}{q}\right)e^{1/q}{\rm Ei}\left(-\frac{1}{q}\right)\right].\end{aligned} \quad (60)$$

Then under the condition $D>1$ ($\Delta>\hbar\omega_c$) we arrive at

$$\begin{aligned}\delta_{T,l=0}^{\rm expl}\mathcal{F}(a,T)&\approx-\alpha_0\frac{\alpha(k_BT)^2}{a^2\tilde v_F^2\hbar c}e^{-\frac{\Delta-2\mu}{2k_BT}}(1-4q)\\ &\approx-\alpha_0\frac{\alpha(k_BT)^2}{a^2\tilde v_F^2\hbar c}e^{-\frac{\Delta-2\mu}{2k_BT}}.\end{aligned} \quad (61)$$

This is quite different behavior at low T than that obtained in Eq. (30) for the thermal correction $\delta_T^{\rm impl}\mathcal{F}$ under the condition $\Delta>2\mu$.

Now we turn to the case $\Delta<2\mu$ for the thermal correction $\delta_{T,l=0}^{\rm expl}\mathcal{F}$. In this case the thermal correction $\delta_T\tilde\Pi_{00,0}$ is given by

$$\delta_T\tilde\Pi_{00,0}(y,T,\Delta,\mu)=\tilde\Pi_{00,0}^{(1)}(y,T,\Delta,\mu)-\tilde\Pi_{00,0}^{(1)}(y,0,\Delta,\mu), \quad (62)$$

where $\tilde{\Pi}_{00,0}^{(1)}$ is defined in Eqs. (8)–(10). For $l = 0$ one has

$$\tilde{\Pi}_{00,0}^{(1)}(y, T, \Delta, \mu) = \frac{4\alpha D}{\tilde{v}_F^2}(I_1 + I_2), \tag{63}$$

where

$$I_1 = \int_1^\infty dt \left(e^{\frac{t\Delta-2\mu}{2k_BT}} + 1\right)^{-1},$$
$$I_2 = \frac{1}{\tilde{v}_F y}\mathrm{Re}\int_1^\infty dt \left(e^{\frac{t\Delta-2\mu}{2k_BT}} + 1\right)^{-1} \frac{D^2t^2 - \tilde{v}_F^2y^2}{[\tilde{v}_F^2y^2 - D^2(t^2-1)]^{1/2}}. \tag{64}$$

Similar to the case of $\Delta > 2\mu$, the first exponential term on the right-hand side of Eq. (9) leads to additional exponentially decreasing factors when the temperature vanishes. For this reason, we do not consider it below. Thus, according to Eqs. (62)–(64), the thermal correction to the polarization tensor takes the form

$$\begin{aligned}
&\delta_T\tilde{\Pi}_{00,0}(y, T, \Delta, \mu) \\
&\quad = \frac{4\alpha D}{\tilde{v}_F^2}\left[\int_1^\infty dt\left(e^{\frac{t\Delta-2\mu}{2k_BT}} + 1\right)^{-1} - \int_1^{2\mu/\Delta} dt + I_2 - \lim_{T\to 0} I_2\right] \\
&\quad = \frac{4\alpha}{\tilde{v}_F^2} e^{-\frac{2\mu-\Delta}{2k_BT}}\left(\frac{2k_BT}{\hbar\omega_c} - 1\right) \\
&\quad \approx -\frac{4\alpha}{\tilde{v}_F^2} e^{-\frac{2\mu-\Delta}{2k_BT}}
\end{aligned} \tag{65}$$

at sufficiently low temperature.

Substituting Eq. (65) in Eq. (52) with $l = 0$ and taking into account that $\tilde{\Pi}_{00,0}(y, 0, \Delta, \mu) = Q_0$, where Q_0 is defined in Eq. (34), one finds

$$\delta_T r_{\mathrm{TM}}(0, y, T) = -\frac{8\alpha}{\tilde{v}_F^2} e^{-\frac{2\mu-\Delta}{2k_BT}} \frac{y}{(Q_0 + 2y)^2}. \tag{66}$$

Finally from Eqs. (49) and (66) we obtain

$$\begin{aligned}
\delta_{T,l=0}^{\mathrm{expl}}\mathcal{F}(a, T) &= \alpha_0 \frac{\alpha k_BT}{4a^3\tilde{v}_F^2} e^{-\frac{2\mu-\Delta}{2k_BT}} \int_0^\infty dy e^{-y} \frac{4y^3}{(2y + Q_0)^2} \\
&= \alpha_0 \frac{\alpha k_BT}{4a^3\tilde{v}_F^2} e^{-\frac{2\mu-\Delta}{2k_BT}} \left[1 - \frac{Q_0}{4}(4 + Q_0)\right. \\
&\quad \left. - \frac{Q_0^2}{8}(Q_0 + 6)e^{Q_0/2}\mathrm{Ei}\left(-\frac{Q_0}{2}\right)\right].
\end{aligned} \tag{67}$$

By comparing Eqs. (61) and (67), one can conclude that in the case $\Delta < 2\mu$ the thermal correction $\delta_{T,l=0}^{\mathrm{expl}}\mathcal{F}$ at low temperatures again decreases with T exponentially fast.

Let us now consider the last case $\Delta = \mu$. Similar in Sec. III, it can be considered starting from the results obtained for $\Delta > 2\mu$. Now, however, the last transformation in Eq. (54) is not allowed because $\exp[(-\Delta + 2\mu)/(2k_BT)] = 1$. As a result, Eq. (57) should be replaced with

$$\delta_T\tilde{\Pi}_{00,0}(y, T, \Delta, \mu) = \frac{8\alpha}{\tilde{v}_F^2}\frac{k_BT}{\hbar\omega_c}\ln 2. \tag{68}$$

Substituting Eqs. (58) and (68) in Eq. (52), we have

$$\delta_T r_{\mathrm{TM}}(0, y, T) = \frac{4\alpha \ln 2}{\tilde{v}_F^2}\frac{k_BT}{\hbar\omega_c}\frac{1}{y(1 + qy)^2}. \tag{69}$$

Then, from Eq. (49), in place of Eq. (61) we finally obtain

$$\delta_{T,l=0}^{\mathrm{expl}}\mathcal{F}(a, T) = -\alpha_0 \frac{\alpha \ln 2 (k_BT)^2}{a^2\tilde{v}_F^2\hbar c}, \tag{70}$$

i.e., the same behavior with T as was found for $\delta_T^{\mathrm{impl}}\mathcal{F}$ in the case $\Delta < 2\mu$ [see Eq. (41)].

The results presented in Eqs. (61), (67), and (70) are illustrated in column 3 of Table I.

V. EXPLICIT TEMPERATURE DEPENDENCE OF REFLECTION COEFFICIENTS: SUMMATION OVER THE NONZERO MATSUBARA FREQUENCIES

Here we consider the low-temperature behavior of the last, third, contribution $\delta_{T,l\geq 1}^{\mathrm{expl}}\mathcal{F}$ to the thermal correction in Eq. (23) which is determined by an explicit dependence of the polarization tensor on T in all Matsubara terms with $l \neq 0$. In accordance to Eq. (25), it is given by

$$\begin{aligned}
\delta_{T,l\geq 1}^{\mathrm{expl}}\mathcal{F}(a, T) &= -\alpha_0 \frac{k_BT}{8a^3}\sum_{l=1}^{\infty}\int_{\zeta_l}^\infty dy e^{-y} G(\zeta_l^2, y, T, \Delta, \mu), \\
G(\zeta_l^2, y, T, \Delta, \mu) &= (2y^2 - \zeta_l^2)\delta_T r_{\mathrm{TM}}(\mathrm{i}\zeta_l, y, T) \\
&\quad - \zeta_l^2\delta_T r_{\mathrm{TE}}(\mathrm{i}\zeta_l, y, T).
\end{aligned} \tag{71}$$

An expression for the thermal correction $\delta_T r_{\mathrm{TM}}$ is already given in Eq. (52). To derive a similar expression for $\delta_T r_{\mathrm{TE}}$, we substitute the representation

$$\tilde{\Pi}_l(y, T, \Delta, \mu) = \tilde{\Pi}_l(y, 0, \Delta, \mu) + \delta_T\tilde{\Pi}_l(y, T, \Delta, \mu) \tag{72}$$

in the second formula in Eq. (2) and expand the obtained expression up to the first power in small parameter

$$\frac{\delta_T\tilde{\Pi}_l(y, T, \Delta, \mu)}{\tilde{\Pi}_l(y, T, \Delta, \mu)}. \tag{73}$$

The desired result is given by

$$\delta_T r_{\rm TE}({\rm i}\zeta_l, y, T) = -\frac{2y(y^2-\zeta_l^2)\delta_T\tilde{\Pi}_l(y,T,\Delta,\mu)}{[\tilde{\Pi}_l(y,0,\Delta,\mu)+2y(y^2-\zeta_l^2)]^2}. \tag{74}$$

We start with the case $\Delta > 2\mu$ where, according to Eq. (17), $\delta_T\tilde{\Pi}_{00,l} = \tilde{\Pi}_{00,l}^{(1)}$ and $\delta_T\tilde{\Pi}_l = \tilde{\Pi}_l^{(1)}$ with $\tilde{\Pi}_{00,l}^{(1)}$ and $\tilde{\Pi}_l^{(1)}$ defined in Eqs. (8)–(10). According to Eq. (16), $\tilde{\Pi}_{00,l}(y,0,\Delta,\mu) = \tilde{\Pi}_{00,l}^{(0)}$ and $\tilde{\Pi}_l(y,0,\Delta,\mu) = \tilde{\Pi}_l^{(0)}$, where the right-hand sides of these equations are given by Eqs. (5)–(7), and under the condition $D > 1$ the quantity $\Psi(D/p_l)$ can be replaced with $8p_l/(3D)$ [see Eq. (28)].

Then, in the lowest order of the small parameter p_l/D, Eqs. (52) and (74) take the form

$$\begin{aligned}
\delta_T r_{\rm TM}({\rm i}\zeta_l, y, T) &= \frac{2y\delta_T\tilde{\Pi}_{00,l}(y,T,\Delta,\mu)}{(y^2-\zeta_l^2)(\frac{8\alpha y}{3D}+2)^2} \\
&\approx \frac{y\delta_T\tilde{\Pi}_{00,l}(y,T,\Delta,\mu)}{2(y^2-\zeta_l^2)}, \\
\delta_T r_{\rm TE}({\rm i}\zeta_l, y, T) &= -\frac{2y\delta_T\tilde{\Pi}_l(y,T,\Delta,\mu)}{(y^2-\zeta_l^2)(\frac{8\alpha p_l^2}{3D}+2y)^2} \\
&\approx -\frac{\delta_T\tilde{\Pi}_l(y,T,\Delta,\mu)}{2y(y^2-\zeta_l^2)}.
\end{aligned} \tag{75}$$

Note that we have omitted two small terms, $8\alpha y/(3D)$ and $8\alpha p_l^2/(3D)$, in the denominators because, similar to Eqs. (59)–(61), they lead to the thermal corrections of higher orders which can be neglected in the result. The function G in Eq. (71), which depends on ζ_l^2, can be expanded in the powers of $\zeta_l^2 = (\tau l)^2$:

$$G(\zeta_l^2, y, T, \Delta, \mu) = 2y^2\delta_T r_{\rm TM}(0,y,T) + \zeta_l^2 \frac{\partial G}{\partial\zeta_l^2}\bigg|_{\zeta_l=0} + \cdots. \tag{76}$$

Substituting this expansion in Eq. (71), one obtains

$$\delta_{T,l\geq1}^{\rm expl}\mathcal{F}(a,T) = -\alpha_0\frac{k_BT}{8a^3}(J_1+J_2), \tag{77}$$

where

$$\begin{aligned}
J_1 &= 2\sum_{l=1}^{\infty}\int_{\zeta_l}^{\infty} dy e^{-y}y^2\delta_T r_{\rm TM}(0,y,T), \\
J_2 &= \sum_{l=1}^{\infty}\zeta_l^2\int_{\zeta_l}^{\infty} dy e^{-y}\frac{\partial G}{\partial\zeta_l^2}\bigg|_{\zeta_l=0} + \cdots.
\end{aligned} \tag{78}$$

From Eqs. (57) and (75) we find

$$\delta_T r_{\rm TM}(0,y,T) = \frac{8\alpha k_BTa}{\tilde{v}_F^2\hbar cy}e^{-\frac{\Delta-2\mu}{2k_BT}}. \tag{79}$$

Taking this into account, we rewrite the quantity J_1 in Eq. (78) as

$$\begin{aligned}
J_1 &= \frac{16\alpha k_BTa}{\tilde{v}_F^2\hbar c}e^{-\frac{\Delta-2\mu}{2k_BT}}\sum_{l=1}^{\infty}\int_{\zeta_l}^{\infty} dy e^{-y}y \\
&= \frac{16\alpha k_BTa}{\tilde{v}_F^2\hbar c}e^{-\frac{\Delta-2\mu}{2k_BT}}\left[\frac{1}{e^\tau-1}+\frac{\tau e^\tau}{(e^\tau-1)^2}\right] \\
&\approx \frac{16\alpha k_BTa}{\tilde{v}_F^2\hbar c}e^{-\frac{\Delta-2\mu}{2k_BT}}\frac{2}{\tau} = \frac{8\alpha}{\tilde{v}_F^2\pi}e^{-\frac{\Delta-2\mu}{2k_BT}}.
\end{aligned} \tag{80}$$

As shown in Appendix B, the integral J_2 contains the same exponentially fast decreasing with T factor and differs from Eq. (80) only by the preexponent coefficient. Because of this, using Eq. (80), we obtain from Eq. (77)

$$\delta_{T,l\geq1}^{\rm expl}\mathcal{F}(a,T) \sim -\alpha_0\frac{k_BT}{a^3}e^{-\frac{\Delta-2\mu}{2k_BT}}. \tag{81}$$

It is seen that here the factor in front of the exponent decreases slower than in $\delta_{T,l=0}^{\rm expl}\mathcal{F}$ [see Eq. (61)].

The case $\Delta < 2\mu$ can be considered in a similar manner. Using Eqs. (34) and (52), we have

$$\delta_T r_{\rm TM}({\rm i}\zeta_l, y, T) = \frac{2y(y^2-\zeta_l^2)\delta_T\tilde{\Pi}_{00,l}(y,T,\Delta,\mu)}{[yQ_0+2(y^2-\zeta_l^2)]^2}. \tag{82}$$

Substituting here Eq. (65) and taking into account that under the condition (33) the inequality $Q_0 \gg 1$ holds, one can neglect by $2y$ as compared to Q_0 and obtain

$$\delta_T r_{\rm TM}(0,y,T) = -\frac{8\alpha}{\tilde{v}_F^2Q_0^2}e^{-\frac{2\mu-\Delta}{2k_BT}}y. \tag{83}$$

Then the quantity J_1 defined in Eq. (78) is

$$\begin{aligned}
J_1 &= -\frac{16\alpha}{\tilde{v}_F^2Q_0^2}e^{-\frac{2\mu-\Delta}{2k_BT}}\sum_{l=1}^{\infty}\int_{\zeta_l}^{\infty} dy e^{-y}y^3 \\
&= -\frac{16\alpha}{\tilde{v}_F^2Q_0^2}e^{-\frac{2\mu-\Delta}{2k_BT}}\left[\tau^3\frac{e^\tau(1+4e^\tau+e^{2\tau})}{(e^\tau-1)^4}\right. \\
&\qquad \left. + 3\tau^2\frac{e^\tau(1+e^\tau)}{(e^\tau-1)^3} + 6\tau\frac{e^\tau}{(e^\tau-1)^2} + \frac{6}{e^\tau-1}\right] \\
&\approx -\frac{16\alpha}{\tilde{v}_F^2Q_0^2}e^{-\frac{2\mu-\Delta}{2k_BT}}\frac{24}{\tau} = -\frac{96\alpha\hbar c}{\tilde{v}_F^2Q_0^2\pi ak_BT}e^{-\frac{2\mu-\Delta}{2k_BT}}.
\end{aligned} \tag{84}$$

Similar to Appendix B, it can be shown that the integral J_2 leads to the same, up to a factor, dependence on T, as in Eq. (84). Thus, from Eq. (77) one finds

$$\delta_{T,l\geq1}^{\rm expl}\mathcal{F}(a,T) \sim \alpha_0\frac{\hbar c}{a^4}e^{-\frac{2\mu-\Delta}{2k_BT}}. \tag{85}$$

This dependence should be compared with that given by Eq. (81) for the case $\Delta > 2\mu$.

Now we consider the behavior of $\delta_{T,l\geq 1}^{\text{expl}}\mathcal{F}$ at low temperature in the case $\Delta = 2\mu$. Similar to the correction $\delta_{T,l=0}^{\text{expl}}\mathcal{F}$ in Sec. IV, this behavior can be investigated using the results obtained for $\Delta > 2\mu$. For this purpose, we take into account that $\Delta = 2\mu$ and from the next to last transformation in Eq. (65) obtain

$$\delta_T \tilde{\Pi}_{00,0}(y, T, \Delta, \mu) = \frac{8\alpha k_B T}{\tilde{v}_F^2 \hbar \omega_c} \ln 2. \tag{86}$$

Then from Eq. (75) we have

$$\delta_T r_{\text{TM}}(0, y, T) = \frac{8\alpha k_B T}{\tilde{v}_F^2 \hbar c} \frac{\ln 2}{y}. \tag{87}$$

Repeating the same derivations as in the case $\Delta > 2\mu$, one arrives at

$$J_1 = \frac{16\alpha k_B T a \ln 2}{\tilde{v}_F^2 \hbar c} \frac{2}{\tau} = \frac{8\alpha \ln 2}{\tilde{v}_F^2 \pi} \tag{88}$$

and for the thermal correction $\delta_{T,l\geq 1}^{\text{expl}}\mathcal{F}$ for $\Delta = 2\mu$ finally finds

$$\delta_{T,l\geq 1}^{\text{expl}}\mathcal{F}(a, T) \sim -\alpha_0 \frac{k_B T}{a^3}. \tag{89}$$

The results given by Eqs. (81), (85), and (89) are presented in column 4 of Table I. A summary of columns 2, 3, and 4 in column 5 demonstrates the leading term in the asymptotic behavior of the thermal correction to the Casimir-Polder energy at low T for any relationship between Δ and 2μ.

It is seen that Eq. (89) differs fundamentally from the behaviors of all thermal corrections considered above. According to the obtained results, in the cases $\Delta > 2\mu$ and $\Delta < 2\mu$ the Casimir-Polder entropy

$$S(a, T) = -\frac{\partial \mathcal{F}(a, T)}{\partial T}, \tag{90}$$

where the Casimir-Polder free energy $\mathcal{F}(a, T)$ is defined in Eqs. (1) and (11), vanishes with vanishing T. In the case $\Delta = 2\mu$ the contribution to the entropy determined by the thermal corrections $\delta_T^{\text{impl}}\mathcal{F}$ and $\delta_{T,l=0}^{\text{expl}}\mathcal{F}$ vanishes with vanishing temperature

$$-\lim_{T\to 0} \frac{\partial}{\partial T} [\delta_T^{\text{impl}}\mathcal{F} + \delta_{T,l=0}^{\text{expl}}\mathcal{F}] = 0. \tag{91}$$

However, according to Eq. (89), the contribution to the entropy determined by the thermal correction $\delta_{T,l\geq 1}^{\text{expl}}\mathcal{F}$ in the case $\Delta = 2\mu$ gives rise to some kind of entropic anomaly

$$-\lim_{T\to 0} \frac{\partial}{\partial T} \delta_{T,l\geq 1}^{\text{expl}}\mathcal{F}(a, T) \neq 0. \tag{92}$$

As a result, in the case $\Delta = 2\mu$ the entropy at zero temperature is not equal to zero and depends on the parameters of a system which means a violation of the Nernst heat theorem (see column 6 of Table I for the low-temperature behavior of the Casimir-Polder entropy in different cases). These results are discussed in Sec. VI in connection with similar problems of the Casimir physics arising for metallic and dielectric materials.

VI. CONCLUSIONS AND DISCUSSION

In the foregoing, we have found the behavior of the Casimir-Polder free energy and entropy at low temperature for a polarizable atom interacting with real graphene sheet possessing nonzero energy gap and chemical potential. As discussed in Sec. I, this subject is of much fundamental interest in connection with problems arising in Casimir physics when using the commonly accepted local models of the dielectric response for both metallic and dielectric materials. The distinctive feature of graphene is that its nonlocal dielectric response, described by the polarization tensor, is found exactly on the basis of first principles of thermal quantum field theory. At the same time, the dielectric responses of conventional materials, described, e.g., by the Drude or plasma models, are partially the phenomenological ones. They are well confirmed experimentally only for real electromagnetic fields on a mass shell, although in the Lifshitz theory the integration is made over all momenta both on and off a mass shell.

According to our results, the contribution $\delta_T^{\text{impl}}\mathcal{F}$ to the thermal correction to the Casimir-Polder energy, originating from a summation over the Matsubara frequencies using the zero-temperature polarization tensor, behaves as $\sim (k_B T)^5$ and $\sim (k_B T)^2$ at low temperature under the conditions $\Delta > 2\mu$ and $\Delta < 2\mu$, respectively. The contribution $\delta_{T,l=0}^{\text{expl}}\mathcal{F}$ to the Casimir-Polder energy, which is caused by an explicit temperature dependence of the polarization tensor in the zero-frequency Matsubara term, behaves as

$$\delta_{T,l=0}^{\text{expl}}\mathcal{F} \sim \begin{cases} -(k_B T)^2 e^{-\frac{\Delta - 2\mu}{2k_B T}}, & \Delta > 2\mu, \\ k_B T e^{-\frac{2\mu - \Delta}{2k_B T}}, & \Delta < 2\mu. \end{cases}$$

In the case $\Delta = 2\mu$, one has $\delta_{T,l=0}^{\text{expl}}\mathcal{F} \sim -(k_B T)^2$.

The most interesting situation arises for the thermal correction $\delta_{T,l\geq 1}^{\text{expl}}\mathcal{F}$ originating from an explicit temperature dependence of the polarization tensor in the sum of all Matsubara terms with nonzero frequencies. As shown in this paper, a summation over all nonzero Matsubara frequencies reduces by one the power of the leading temperature dependence in each of the cases $\Delta > 2\mu$, $\Delta < 2\mu$, and $\Delta = 2\mu$. As a result, one obtains that

$$\delta_{T,l\geq 1}^{\text{expl}}\mathcal{F}\sim\begin{cases}-k_BTe^{-\frac{\Delta-2\mu}{2k_BT}}, & \Delta>2\mu,\\ e^{-\frac{2\mu-\Delta}{2k_BT}}, & \Delta<2\mu,\end{cases}$$

and $\delta_{T,l\geq 1}^{\text{expl}}\mathcal{F}\sim -k_BT$ for $\Delta=2\mu$.

The above results for all three contributions to the thermal correction combined together lead us to a conclusion that in both cases $\Delta>2\mu$ and $\Delta<2\mu$ the Casimir-Polder free energy and entropy satisfy the Nernst heat theorem. In doing so, the leading terms in the Casimir-Polder free energy at low temperature behave as $\sim(k_BT)^5$ and $(k_BT)^2$ for $\Delta>2\mu$ and $\Delta<2\mu$, respectively. Thus, our results do not support the statement of Ref. [88] that "the first order correction is quadratic over temperature $\sim T^2$." This is true for the case $\Delta<2\mu$ but not for $\Delta>2\mu$ where the total free energy $\mathcal{F}\sim(k_BT)^5$. Also, if the exact equality $\Delta=2\mu$ is valid, the Casimir-Polder free energy is linear in temperature $\mathcal{F}\sim k_BT$. In this case the Casimir-Polder entropy at zero temperature is equal to a nonzero constant depending on the parameters of a system and, thus, the Nernst heat theorem is violated. Note for a pristine graphene where $\mathcal{F}\sim(k_BT)^3$ the Nernst heat theorem is satisfied [87].

As discussed in Sec. I, for dielectrics and metals the models of dielectric response leading to a violation of the Nernst heat theorem also result in contradictions between the theoretical predictions and the experimental data for the Casimir and Casimir-Polder forces. Up to date there is a single experiment on measuring the Casimir interaction between a Au-coated sphere and a graphene sheet deposited on a substrate [94], and its data are in good agreement with theoretical results obtained using the polarization tensor of graphene [95]. In fact the values of Δ and μ for a graphene sample used in the experiment are not known precisely so that from the practical standpoint the equality $\Delta=2\mu$ cannot be satisfied exactly. For comparison purposes, the character of the real part of conductivity of graphene as a function of frequency also changes qualitatively depending on whether $\Delta>2\mu$ or $\Delta<2\mu$ [96], so that the condition $\Delta=2\mu$ defines a singular point.

One can conclude that with the only exception of a physically unrealizable case $\Delta=2\mu$ the Casimir-Polder free energy and entropy for an atom interacting with real graphene sheet characterized by nonzero energy gap and chemical potential satisfy the Nernst heat theorem. This result provides further support to the assumption that the widely known problems in Casimir physics discussed in Sec. I may be connected with the phenomenological character of local response functions used for both metallic and dielectric materials.

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APPENDIX A: BOUND FOR THE CONTRIBUTION TO $\delta_T\tilde{\Pi}_{00,0}$ IN THE CASE $\Delta>2\mu$

In this Appendix, we consider the integral used in Eq. (55) and for $\Delta>2\mu$ and restrict it as follows:

$$\begin{aligned}&\int_1^{f(y)}dt\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1}\frac{D^2t^2-\tilde{v}_F^2y^2}{[\tilde{v}_F^2y^2-D^2(t^2-1)]^{1/2}}\\ &\quad<D^2\int_1^{f(y)}dt\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1}\\ &\quad\times\frac{t^2}{[\tilde{v}_F^2y^2-D^2(t^2-1)]^{1/2}}\equiv I,\end{aligned}\tag{A1}$$

where $f(y)$ is defined in Eq. (56).

The integral on the right-hand side of Eq. (A1) can be integrated by parts

$$\begin{aligned}I=&-\int_1^{f(y)}t\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1}d[\tilde{v}_F^2y^2-D^2(t^2-1)]^{1/2}\\ &=\left(e^{\frac{\Delta-2\mu}{2k_BT}}+1\right)^{-1}\tilde{v}_Fy\\ &\quad+\int_1^{f(y)}d\left[t\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1}\right][\tilde{v}_F^2y^2-D^2(t^2-1)]^{1/2}.\end{aligned}\tag{A2}$$

The square root on the right-hand side of Eq. (A2) only increases when we replace it with $\tilde{v}_Fy$. Then Eq. (A2) transforms to

$$I<\tilde{v}_Fyf(y)\left[e^{\frac{f(y)\Delta-2\mu}{2k_BT}}+1\right]^{-1}.\tag{A3}$$

Now we take into account that, according to Eq. (56),

$$f(y)=\sqrt{1+\frac{\tilde{v}_F^2y^2}{D^2}}\approx 1+\frac{\tilde{v}_F^2y^2}{2D^2}=1+\frac{\tilde{v}_F^2y^2(\hbar\omega_c)^2}{2\Delta^2}\tag{A4}$$

and that for sufficiently low T the inequality $\Delta-2\mu\gg 2k_BT$ holds. Then one can neglect by the unity in Eq. (A3) as compared to the exponent and, substituting Eq. (A4) to its power, obtain

$$I<\frac{\tilde{v}_Fy}{D}\sqrt{D^2+\tilde{v}_F^2y^2}e^{-\frac{\Delta-2\mu}{2k_BT}}e^{-\frac{(\hbar\omega_c\tilde{v}_Fy)^2}{4k_BT\Delta}}.\tag{A5}$$

Multiplying Eqs. (A1) and (A5) by the factor $4\alpha D/(y\tilde{v}_F{}^3)$, we arrive at Eq. (55).

APPENDIX B: ESTIMATION FOR THE CONTRIBUTION TO $\delta_{T,l\geq 1}^{\rm expl}\mathcal{F}$ IN THE CASE $\Delta > 2\mu$

Here, we estimate the contribution J_2 to the thermal correction to the Casimir-Polder free energy (77) defined by the second expression in Eq. (78).

According to Eq. (71), the value of the first derivative of G, entering Eq. (78), is given by

$$\left.\frac{\partial G}{\partial\zeta_l^2}\right|_{\zeta_l=0} = -\delta_T r_{\rm TM}(0,y,T) + 2y^2\left.\frac{\partial}{\partial\zeta_l^2}\delta_T r_{\rm TM}({\rm i}\zeta_l,y,T)\right|_{\zeta_l=0} - \delta_T r_{\rm TE}(0,y,T), \tag{B1}$$

where expressions for the thermal corrections to the reflection coefficients are contained in Eq. (75).

The derivative of the thermal correction $\delta_T r_{\rm TM}$ is calculated using the first expression in Eq. (75),

$$\left.\frac{\partial}{\partial\zeta_l^2}\delta_T r_{\rm TM}({\rm i}\zeta_l,y,T)\right|_{\zeta_l=0} = \frac{1}{2y^3}\delta_T\tilde{\Pi}_{00,0}(y,T,\Delta,\mu) + \frac{1}{2y}\left.\frac{\partial}{\partial\zeta_l^2}\delta_T\tilde{\Pi}_{00,l}(y,T,\Delta,\mu)\right|_{\zeta_l=0}. \tag{B2}$$

Using Eq. (17) and Eqs. (8)–(10), where only the second term contributes in Eq. (9), one obtains at sufficiently low T

$$\left.\frac{\partial}{\partial\zeta_l^2}\delta_T\tilde{\Pi}_{00,l}(y,T,\Delta,\mu)\right|_{\zeta_l=0} = \frac{4\alpha D}{\tilde{v}_F^2}\int_1^\infty dt\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1}\left.\frac{\partial\chi_{00,l}}{\partial\zeta_l^2}\right|_{\zeta_l=0} \approx \frac{b_1}{y^4}\frac{k_BT}{\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}, \tag{B3}$$

where the numerical value of the constant b_1 is of no concern for us now.

As to the thermal correction $\delta_T\tilde{\Pi}_{00.0}$ in Eq. (B2), at low T it is contained in Eq. (57) and can be written in the form

$$\delta_T\tilde{\Pi}_{00,0}(y,T,\Delta,\mu) = b_2\frac{k_BT}{\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}. \tag{B4}$$

Substituting Eqs. (B3) and (B4) in Eq. (B2), one obtains

$$\left.\frac{\partial}{\partial\zeta_l^2}\delta_T r_{\rm TM}({\rm i}\zeta_l,y,T)\right|_{\zeta_l=0} = \frac{k_BT}{2\hbar\omega_c}\left(\frac{b_1}{y^5}+\frac{b_2}{y^3}\right)e^{-\frac{\Delta-2\mu}{2k_BT}}. \tag{B5}$$

Now we return to Eq. (B1) where the first term on the right-hand side is found from Eqs. (75) and (B4):

$$\delta_T r_{\rm TM}(0,y,T) = \frac{b_2}{2y}\frac{k_BT}{\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}. \tag{B6}$$

The remaining term $\delta_T r_{\rm TE}(0,y,T)$ in Eq. (B1) is given by the second expression in Eq. (75) where, in accordance to Eq. (17), the quantity $\delta_T\tilde{\Pi}_0$ is expressed by Eq. (5). The following result is found with the help of Eqs. (8)–(10):

$$\delta_T r_{\rm TE}(0,y,T) = \frac{4\alpha D^3 y}{\tilde{v}_F}\int_1^{f(y)} dt\left(e^{\frac{t\Delta-2\mu}{2k_BT}}+1\right)^{-1} \times\frac{t^2-1}{[\tilde{v}_F^2y^2-D^2(t^2-1)]^{1/2}}, \tag{B7}$$

where $f(y)$ is defined in Eq. (56). This quantity is similar to that considered in Appendix A. By repeating the derivations of Appendix A, it is easy to see that it contains an exponentially decreasing with T factor in addition to that one contained in Eq. (B6). Thus, we can neglect by the quantity (B7) in Eq. (B1) as compared to other terms.

Using Eqs. (B5) and (B6), one obtains from Eq. (B1)

$$\left.\frac{\partial G}{\partial\zeta_l^2}\right|_{\zeta_l=0} = \frac{k_BT}{2\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}\left(\frac{b_2}{y}+\frac{2b_1}{y^3}\right). \tag{B8}$$

Substituting this equation to the second expression in Eq. (78), we find

$$J_2 = \frac{k_BT}{2\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}\sum_{l=1}^{\infty}\int_{\zeta_l}^{\infty}dy\,e^{-y}\left(\frac{b_2}{y}+\frac{2b_1}{y^3}\right)\zeta_l^2+\cdots. \tag{B9}$$

Introducing the integration variable $v = y/\zeta_l$, one obtains from Eq. (B9)

$$\begin{aligned} J_2 &= \frac{k_BT}{2\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}\int_1^\infty dv\left[\frac{b_2}{v}\sum_{l=1}^{\infty}\zeta_l^2e^{-v\zeta_l}+\frac{2b_1}{v^3}\sum_{l=1}^{\infty}e^{-v\zeta_l}\right]+\cdots \\ &= \frac{2k_BT}{\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}\left[b_2\tau^2\int_1^\infty\frac{dv\,e^{\tau v}(e^{\tau v}+1)}{v(e^{\tau v}-1)^3}+2b_1\int_1^\infty\frac{dv}{v^3(e^{\tau v}-1)}\right]+\cdots \\ &= \frac{k_BT}{\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}\frac{b_1+b_2}{\tau}\int_1^\infty\frac{dv}{v^4}+\cdots = \frac{k_BT}{\hbar\omega_c}e^{-\frac{\Delta-2\mu}{2k_BT}}\frac{b_1+b_2}{3\tau}+\cdots\sim e^{-\frac{\Delta-2\mu}{2k_BT}}+\cdots. \end{aligned} \tag{B10}$$

Thus, a summation in nonzero l again results in the additional factor ~$1/\tau$. The same holds for all expansion terms in the higher powers of ζ_l notated by dots in Eq. (B10). Thus, J_2 contains the same exponentially decreasing with T factor as J_1, and the result (81) remains valid with account of J_2.

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