Problems in the theory of the thermal Casimir force between dielectrics and semiconductors

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Abstract
The application of the Lifshitz theory to describe the thermal Casimir force
between dielectrics and semiconductors is considered. It is shown that
for all true dielectrics (i.e., for all materials having zero conductivity at
zero temperature) the inclusion of a nonzero conductivity arising at nonzero
temperature into the model of dielectric response leads to the violation of the
Nernst heat theorem. This result refers equally to simple insulators, intrinsic
semiconductors, Mott–Hubbard dielectrics and doped semiconductors with
doping concentration below a critical value. We demonstrate that in the
insulator–metal transition the Casimir free energy changes abruptly irrespective
of whether the conductivity changes continuously or discontinuously. The
application of the Lifshitz formula to polar dielectrics results in a large thermal
correction that is linear in temperature. A rule is formulated on how to apply
the Lifshitz theory to real materials in agreement with thermodynamics and
experiment.

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1. Introduction

The last ten years are marked by quick progress in experimental investigation of the Casimir
effect [1]. The early stages of this process (reflected in review [2]) were followed by the
measurement of the Casimir force in the original configuration of two parallel plates [3]
and first experimental demonstrations of the lateral Casimir force. Thereafter the precise
measurements by using the micromechanical torsional oscillator [5–7] and first experiments
on measuring the Casimir force between metal and semiconductor test bodies [8, 9] were
performed. It was demonstrated also that the force between metal and semiconductor can be
controlled by the illumination of a semiconductor plate with laser pulses [10].

Intensive experimental work created demands theoretical computations of the Casimir
force between real material bodies used in the laboratory setups. The Casimir effect arises

due to quantum fluctuations of the electromagnetic field [11]. The recognized basic theory of both the van der Waals and Casimir force is the Lifshitz theory [12, 13]. In the framework of this theory, material properties are described by the dielectric permittivity $\varepsilon(\omega, T)$ depending on the frequency ω and the temperature T. The free energy per unit area of the van der Waals and Casimir interaction between two thick plane parallel plates at a separation a in thermal equilibrium is given by [2, 12, 13]

$$\mathcal{F}(a, T) = \frac{k_B T}{2\pi} \sum_{l=0}^{\infty} \left(1 - \frac{1}{2}\delta_{0l}\right) \int_0^{\infty} k_\perp \, \mathrm{d}k_\perp$$
$$\times \left\{ \ln\left[1 - r_{\mathrm{TM}}^2(\mathrm{i}\xi_l, k_\perp)\,\mathrm{e}^{-2aq_l}\right] + \ln\left[1 - r_{\mathrm{TE}}^2(\mathrm{i}\xi_l, k_\perp)\,\mathrm{e}^{-2aq_l}\right]\right\}. \quad (1)$$

Here k_B is the Boltzmann constant, $\xi_l = 2\pi k_B T l/\hbar$ with $l = 0, 1, 2, \ldots$ are the Matsubara frequencies and the reflection coefficients for the two independent polarizations of the electromagnetic field (transverse magnetic and transverse electric) are given by

$$r_{\mathrm{TM}}(\mathrm{i}\xi_l, k_\perp) = \frac{\varepsilon_l q_l - k_l}{\varepsilon_l q_l + k_l}, \qquad r_{\mathrm{TE}}(\mathrm{i}\xi_l, k_\perp) = \frac{k_l - q_l}{k_l + q_l},$$
$$q_l = \sqrt{k_\perp^2 + \frac{\xi_l^2}{c^2}}, \qquad k_l = \sqrt{k_\perp^2 + \varepsilon_l \frac{\xi_l^2}{c^2}}, \qquad \varepsilon_l = \varepsilon(\mathrm{i}\xi_l, T) \quad (2)$$

($k_\perp = |\mathbf{k}_\perp|$ is the projection of a wave vector on the plane of the plates). It should be noted that all Matsubara frequencies with $l \geqslant 1$ are rather high at all accessible temperatures. As an example, at room temperature $T = 300$ K it holds

$$\xi_1 = 2.47 \times 10^{14}\ \mathrm{rads}^{-1}, \qquad \xi_l = l\xi_1. \quad (3)$$

However, the application of the Lifshitz theory for the calculation of the thermal Casimir force between real metals leads to serious problems. It was shown that the usual description of a metal by means of the Drude dielectric function results in the violation of the third principle of thermodynamics (the Nernst heat theorem) in the case of perfect crystal lattice [14] and in contradictions with experiment [5–7] (see review in [15]). The application of the Lifshitz theory at nonzero temperature to dielectric materials taking into account their conductivity at zero frequency also leads to the violation of Nernst's theorem [16, 17]. Leaving aside the case of metals (see [18, 19] for further discussion), we concentrate in this paper on the problems of the Lifshitz theory arising when it is applied to real dielectrics and semiconductors.

Below we demonstrate that for all true dielectrics (i.e., for materials having zero conductivity at $T = 0$) the account of nonzero conductivity arising at $T > 0$ leads to a violation of the Nernst heat theorem in the Lifshitz theory. In particular we show that for doped semiconductors with sufficiently low doping concentration (i.e., lower than the critical concentration above which the conductivity is of metallic type) the account of conductivity at zero frequency violates the Nernst heat theorem as well. For doped Si samples with low doping concentration the inclusion of conductivity arising at $T > 0$ has been rejected experimentally at 95% confidence level [10]. According to the obtained results, in the insulator–metal transition the Casimir free energy and force change abruptly irrespective of whether the conductivity changes continuously or discontinuously. The account of orientation polarization in polar dielectrics results in a large thermal correction, being linear in the temperature, to the Casimir force at separations of the order of hundreds of nanometers. Arguments are presented that this effect is nonphysical.

The paper is organized as follows. In section 2 we discuss the main characteristic features of simple dielectrics, metals, semimetals and doped semiconductors. Section 3 is devoted to the violation of the Nernst theorem for all materials whose conductivity at zero temperature is

equal to zero if at $T \neq 0$ their conductivity is included into the model of dielectric response in the Lifshitz theory. The Casimir effect in insulator–metal transition is considered in section 4. In section 5 we discuss problems which arise for polar dielectrics. Section 6 contains our conclusions and discussion.

2. Free charge carriers in different materials

It is common knowledge that at nonzero temperature all materials contain some amount of free charge carriers. For materials with very low charge carrier density (insulators) the dielectric permittivity is usually represented in the form

$$\varepsilon(\omega) = 1 + \sum_j \frac{g_j}{\omega_j^2 - \omega^2 - i\gamma_j\omega}, \tag{4}$$

where $\omega_j \neq 0$ are the oscillator frequencies, g_j are the oscillator strengths and γ_j are the damping parameters (note that in general case the parameters of oscillators may depend on temperature but this minor dependence can be neglected). From (4) the dielectric permittivity at zero frequency is given by

$$\varepsilon_0 \equiv \varepsilon(0) = 1 + \sum_j \frac{g_j}{\omega_j^2} < \infty. \tag{5}$$

Equation (4) does not take free charge carriers into account. This means that in this simple model the conductivity of the insulator is assumed to be equal to zero at any temperature. However, at $T \neq 0$ all insulators possess some nonzero conductivity, $\sigma_0 \neq 0$, and respective finite resistivity $\rho = 1/\sigma_0$. As an example, at room temperature ($T = 300$ K) resistivity of different insulators can vary over a wide range from about 10^8 to about 10^{17} Ω cm. Resistivity of metals varies in the range from 10^{-6} to about 10^{-4} Ω cm. By convention the range of resistivities from about 10^{-3} to 10^7 Ω cm is attributed to semiconductors. The dielectric permittivity of insulators and semiconductors at nonzero temperature can be represented in the form [20]

$$\tilde{\varepsilon}(\omega, T) = \varepsilon(\omega) + i\frac{4\pi\sigma_0(T)}{\omega}, \tag{6}$$

where $\varepsilon(\omega)$ is given in (4).

The characteristic properties of different materials are determined by the behavior of the density N of one-electron states as a function of energy E_e at zero temperature [21]. As was stated in [21], the most fundamental property of true dielectrics separating them from metals is that the former possess zero conductivity, $\sigma_0 = 0$, at zero temperature. In figure 1(a) we present the typical functional form of $N(E_e)$ for insulators and intrinsic (i.e., undoped) semiconductors [22]. In this figure, all states in the shaded region are filled (this is the valence band) and all states in the nonshaded region are empty (the conduction band). The Fermi energy, E_F, separates filled and empty states. As is seen in figure 1(a), here $N(E_F) = 0$. From this it follows that $\sigma_0(T = 0) = 0$ for both insulators and intrinsic semiconductors. The universal behavior of their conductivity at $T \neq 0$ is given by

$$\sigma_0(T) \sim \exp\left(-\frac{\Delta}{2k_BT}\right), \tag{7}$$

where Δ is the band gap. By convention the material is called insulator if $\Delta \geqslant$ 2–3 eV and intrinsic semiconductor if $\Delta <$ 2–3 eV [22]. For comparison in figure 2(b) we show schematically the typical functional form of $N(E_e)$ for metals. Here, $N(E_F) \neq 0$ and the conductivity at zero temperature is not equal to zero, $\sigma_0(T = 0) \neq 0$.
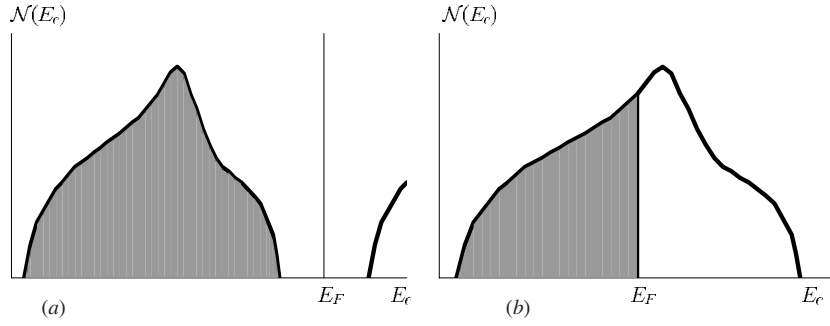
Figure 1. Density of states N (*a*) for insulators and intrinsic semiconductors and (*b*) for metals as a function of energy E_e. The filled states are shaded, E_F is the Fermi energy.
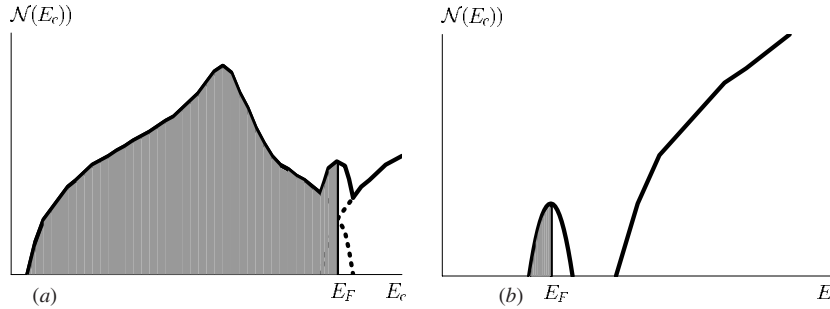

Figure 2. Density of states N (*a*) for semimetals and Mott–Hubbard dielectrics and (*b*) for *n*-type semiconductors where only the impurity band is shown. The filled states are shaded, E_F is the Fermi energy.

There are, however, materials which are characterized by a nonzero density of states at $E = E_F$, but have zero conductivity at zero temperature. To illustrate this we consider the typical behavior of the density of states at $T = 0$, as shown in figure 2(*a*). Here, the valence and conduction bands overlap and the resulting band is restricted by the solid line. The band structure of figure 2(*a*) in fact describes two different types of materials: semimetals and Mott–Hubbard dielectrics [22]. For semimetals it holds $N(E_F) \neq 0$ and $\sigma_0(T = 0) \neq 0$ like for usual metals [23]. As to Mott–Hubbard dielectrics, they are characterized by $N(E_F) \neq 0$ but $\sigma_0(T = 0) = 0$. This is explained by the fact that for such materials the one-electron approximation works rather badly and electron correlations play an important role [22]. At $T > 0$ Mott–Hubbard dielectrics have some nonzero conductivity that depends on the temperature as

$$\sigma_0(T) \sim \exp\left(-\frac{C}{k_B T}\right), \tag{8}$$

where the parameter C has a different physical meaning than Δ in (7).

One more type of materials are doped semiconductors. They are obtained from intrinsic semiconductors by the inclusion of some foreign atoms in their crystal lattice. The typical density of states for these materials is shown in figure 2(*b*) (*n*-type semiconductor), where the first zone containing the Fermi energy is the impurity band. The second (empty) zone is the conduction band of the intrinsic semiconductor. The valence band of the intrinsic semiconductor is not shown (it is the same as in figure 1(*a*)). As is seen in figure 2(*b*),

$N(E_F) \neq 0$. It is important that for doped semiconductors $\sigma_0(T = 0) \neq 0$ for doping concentration $n > n_{\mathrm{cr}}$, where n_{cr} is the so-called *critical* doping concentration, and $\sigma_0(T = 0) = 0$ for $n < n_{\mathrm{cr}}$. This can be explained as follows [24]. In the perfect crystal lattice of an intrinsic semiconductor delocalization of electrons is caused by the periodicity of the lattice. Impurity centers are distributed randomly. The one-electron states which form the impurity zone are of different nature depending on whether $n < n_{\mathrm{cr}}$ or $n > n_{\mathrm{cr}}$. If $n < n_{\mathrm{cr}}$, electrons are localized in the vicinity of impurity centers. For the localized electron states, conductivity at $T = 0$ is equal to zero (in the same way as for the delocalized electron states due to the perfect lattice of an intrinsic semiconductor). However, when $n > n_{\mathrm{cr}}$ the electron states of impurities overlap and due to this become delocalized. Thus, they are of the same kind as electron states in metals leading to $\sigma_0(T = 0) \neq 0$. An example of this situation is given by Si doped with P. For this case $n_{\mathrm{cr}} \approx 3.7 \times 10^{18}$ cm^{-3}. If $n < n_{\mathrm{cr}}$ the conductivity of P-doped Si at $T = 0$ is equal to zero. At sufficiently low T it is given by (8) with some constant C [24].

We emphasize that for all materials whose conductivity at $T = 0$ is equal to zero (insulators, intrinsic semiconductors, Mott–Hubbard dielectrics, doped semiconductors with $n < n_{\mathrm{cr}}$) the low-temperature behavior of their conductivity obeys equations (7), (8), i.e., σ_0 vanishes exponentially fast with the temperature.

3. Thermodynamic test for the Lifshitz theory of the Casimir force between dielectrics and semiconductors

Here we consider the low-temperature asymptotic behavior of the Lifshitz formula (1), (2) for the Casimir free energy in combination with the dielectric permittivities (4) and (6). We also calculate the respective Casimir entropy and check whether or not the Nernst heat theorem is satisfied.

It is convenient to introduce the dimensionless variables

$$y = 2q_l a, \qquad \zeta_l = \frac{\xi_l}{\omega_c} = \tau l, \qquad \omega_c = \frac{c}{2a}, \qquad \tau = \frac{4\pi k_B a T}{\hbar c}. \qquad (9)$$

By using the Abel–Plana formula [2]

$$\sum_{l=0}^{\infty} \left(1 - \frac{1}{2}\delta_{l0}\right) F(l) = \int_0^{\infty} F(t)\,\mathrm{d}t + \mathrm{i} \int_0^{\infty} \mathrm{d}t \frac{F(\mathrm{i}t) - F(-\mathrm{i}t)}{\mathrm{e}^{2\pi t} - 1}, \qquad (10)$$

the Casimir free energy can be represented as the sum of the energy at $T = 0$ and the thermal correction to it

$$\mathcal{F}(a, T) = E(a) + \Delta_T \mathcal{F}(a, T), \qquad (11)$$

where

$$
\begin{aligned}
E(a) &= \frac{\hbar c}{32\pi^2 a^3} \int_0^{\infty} \mathrm{d}\zeta \int_{\zeta}^{\infty} \mathrm{d}y\, f(\zeta, y), \\
f(\zeta, y) &= y\left\{ \ln\left[1 - r_{\mathrm{TM}}^2(\mathrm{i}\zeta, y)\,\mathrm{e}^{-y}\right] + \ln\left[1 - r_{\mathrm{TE}}^2(\mathrm{i}\zeta, y)\,\mathrm{e}^{-y}\right] \right\}, \\
\Delta_T \mathcal{F}(a, T) &= \frac{\mathrm{i}\hbar c \tau}{32\pi^2 a^3} \int_0^{\infty} \mathrm{d}t \frac{F(\mathrm{i}t\tau) - F(-\mathrm{i}t\tau)}{\mathrm{e}^{2\pi t \tau} - 1}, \\
F(x) &\equiv \int_x^{\infty} \mathrm{d}y\, f(x, y).
\end{aligned}
\qquad (12)
$$

The reflection coefficients expressed in terms of dimensionless variables are given by

$$r_{\mathrm{TM}}(\mathrm{i}\zeta, y) = \frac{\varepsilon y - \sqrt{y^2 + \zeta^2(\varepsilon - 1)}}{\varepsilon y + \sqrt{y^2 + \zeta^2(\varepsilon - 1)}}, \qquad r_{\mathrm{TE}}(\mathrm{i}\zeta, y) = \frac{\sqrt{y^2 + \zeta^2(\varepsilon - 1)} - y}{\sqrt{y^2 + \zeta^2(\varepsilon - 1)} + y}. \qquad (13)$$

Now we substitute ε from (4) into the reflection coefficients (13). To obtain the asymptotic behavior of the thermal correction, $\Delta\mathcal{F}(a, T)$, at $\tau \ll 1$, we expand the function $f(x, y)$ in (12) in powers of $x = t\tau$. The subsequent integration of this expansion with respect to y from x to infinity results in

$$F(ix) - F(-ix) = \frac{8ibx}{\varepsilon_0^2 - 1}\operatorname{Li}_2(r_0^2) + \frac{i\pi}{2}r_0^2(\varepsilon_0 + 1)x^2 - 240\,iC_4x^3 + O(x^4), \tag{14}$$

where $\operatorname{Li}_n(z)$ is the polylogarithm function, C_4 is some coefficient and the following notations are used:

$$b = b(a) = \sum_j \frac{g_j\gamma_j\omega_c}{\omega_j^4}, \qquad r_0 = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 1}. \tag{15}$$

Substituting (14) into (12) and performing integration with respect to t from zero to infinity, we obtain

$$\mathcal{F}(a, T) = E(a) - \frac{\hbar c}{32\pi^2 a^3}\left[\frac{b\operatorname{Li}_2(r_0^2)}{3(\varepsilon_0^2 - 1)}\tau^2 + \frac{\zeta(3)r_0^2(\varepsilon_0 + 1)}{8\pi^2}\tau^3 - C_4\tau^4 + O(\tau^5)\right], \tag{16}$$

where $\zeta(z)$ is the Riemann zeta function. The explicit expression for the coefficient C_4 can be found as in [16] by considering the Lifshitz formula for the Casimir pressure. In the case $\gamma_j = 0$ the result is

$$C_4 = \frac{1}{720}\left(\varepsilon_0^{1/2} - 1\right)\left(\varepsilon_0^2 + \varepsilon_0^{3/2} - 2\right). \tag{17}$$

From (16) the Casimir entropy is given by the expression

$$S(a, T) = -\frac{\partial\mathcal{F}(a, T)}{\partial T} = \frac{k_B\tau}{8\pi a^2}\left[\frac{2b\operatorname{Li}_2(r_0^2)}{3(\varepsilon_0^2 - 1)} + \frac{3\zeta(3)r_0^2(\varepsilon_0 + 1)}{8\pi^2}\tau - 4C_4\tau^2 + O(\tau^3)\right]. \tag{18}$$

As is seen from (18), $S(a, T)$ goes to zero when T goes to zero, i.e., the Nernst heat theorem is satisfied when the dielectric permittivity is given by (4) with a finite static value (5).

Now we take into account the conductivity of true dielectrics that arises at $T > 0$. In this case we should replace the dielectric permittivity (4) with the dielectric permittivity (6), where at low temperatures the conductivity $\sigma_0(T)$ decreases exponentially with T as given in (7), (8). We recall that this universal behavior is relevant to all materials with $\sigma_0(T = 0) = 0$, i.e., for insulators, intrinsic semiconductors, Mott–Hubbard dielectrics and doped semiconductors with $n < n_{\rm cr}$. From (6) it follows

$$\tilde{\varepsilon}_l = \tilde{\varepsilon}(i\xi_l, T) = \varepsilon_l + \frac{\beta(T)}{l}, \tag{19}$$

where $\beta(T) = 2\hbar\sigma_0(T)/(k_B T)$. From (7), (8) we conclude that at sufficiently low T it holds $\beta(T) \ll 1$ for all materials with $\sigma_0(T = 0) = 0$. Repeating the above calculation of the Casimir free energy at low temperatures using the Lifshitz formula, one arrives at the result (see [16] for details)

$$\tilde{\mathcal{F}}(a, T) = \mathcal{F}(a, T) - \frac{k_B T}{16\pi a^2}\left[\zeta(3) - \operatorname{Li}_3(r_0^2) + R(\tau)\right], \tag{20}$$

where $\mathcal{F}(a, T)$ is given in (16) and $R(\tau)$ decreases exponentially when T vanishes. From (20) the Casimir entropy at $T = 0$ is given by

$$\tilde{S}(a, 0) = \frac{k_B}{16\pi a^2}\left[\zeta(3) - \operatorname{Li}_3(r_0^2)\right] > 0 \tag{21}$$
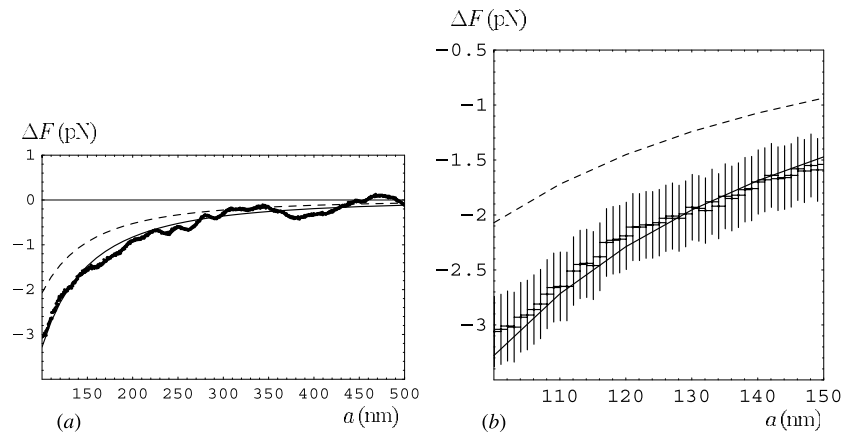
in violation of the Nernst theorem.

Figure 3. Differences of the Casimir forces between an Au sphere and a Si plate illuminated with laser pulses with light on and off versus separation. Solid and dashed lines represent theoretical differences computed at $T = 300$ K disregarding and taking into account the conductivity of Si plate in the absence of light. Mean experimental differences are shown as dots. (*a*) Complete data over the entire measurement range. (*b*) Data over a more narrow separation interval with experimental errors determined at 95% confidence level shown as crosses.

Thus, inclusion of nonzero conductivity arising at $T > 0$ into the model of dielectric response for all materials possessing zero conductivity at zero temperature leads to contradictions between the Lifshitz theory and thermodynamics. That is why for true dielectrics conductivity must be disregarded in theoretical computations. This conclusion has been already confirmed experimentally in the measurements of the difference Casimir force between an Au sphere and a Si plate illuminated with laser pulses [10]. In figure 3(*a*) we plot the difference of the Casimir force between a sphere and a plate, ΔF, when the laser light is on and off, as a function of separation. Mean experimentally measured difference data are shown as dots. Solid line shows the theoretical results computed using the dielectric permittivity (4) in the absence of laser pulse (in this case $n < n_{\mathrm{cr}}$). Dashed line was obtained using the dielectric permittivity (6) in the absence of laser light, i.e., taking conductivity into account. As is seen in figure 3(*a*), the solid line is in good agreement with data, whereas the dashed line is experimentally excluded. For illustrative purposes, the same data and theories are presented over a more narrow separation interval in figure 3(*b*) with indication of experimental errors found at 95% confidence level. The solid and dashed lines have the same meaning as in figure 3(*a*) representing the theoretical force differences computed using the dielectric permittivities (4) and (6), respectively, in the absence of laser light. It is clearly seen that a theory taking into account the conductivity of doped Si with doping concentration below its critical value is experimentally excluded. But, a theory which disregards this conductivity of Si is in good agreement with data.

4. The Casimir effect in the insulator–metal transition

Insulator–metal transition is the phase transition leading to a change of the character (and magnitude) of conductivity with the change of temperature, pressure, magnetic field or composition. A familiar example is an abrupt transition from the monoclinic phase at room temperature to tetragonal phase at $T > 340$ K in VO_2 [25]. Such a transition leads to a change

of conductivity of order 10^4. Recently an experiment has been proposed [26] measuring the change of the Casimir force acting between an Au coated sphere and a VO_2 film deposited on sapphire substrate which undergoes the insulator–metal transition with the increase of temperature. Before the phase transition, in accordance with the results of section 3, the conductivity properties of VO_2 should not be included in the model of dielectric response. Thus, the results of this experiment could be used as one more fundamental test of the Lifshitz theory in application to real materials.

One more example is the insulator–metal phase transition which takes place in n-Si doped by P with the increase of doping concentration. In this case the critical concentration is $n_{cr} \approx 3.7 \times 10^{18}$ cm^{-3} [24]. We consider the doping concentrations $n_1 \approx 2.5 \times 10^{18}$ cm^{-3} (the respective resistivity is $\rho_1 \approx 2 \times 10^{-2}$ Ω cm [27]) just before the phase transition and $n_2 \approx 5 \times 10^{18}$ cm^{-3} ($\rho_2 \approx 1 \times 10^{-2}$ Ω cm) after the phase transition. It is easily seen that this transition has a pronounced effect only on the zero contribution to the Lifshitz formula (1) and practically does not influence the contributions of all Matsubara frequencies with $l \geqslant 1$. It is interesting to find the difference between the Casimir free energies after, $\mathcal{F}_2(a, T)$, and before, $\mathcal{F}_1(a, T)$, the phase transition in the interaction of metal and Si plates. Using the calculation procedure justified in section 3 both thermodynamically and experimentally (i.e., disregarding the conductivity of Si plate before and taking it into account after the phase transition) we arrive at

$$\mathcal{F}_2(a, T) - \mathcal{F}_1(a, T) = -\frac{k_B T}{16\pi a^2}[\zeta(3) - \mathrm{Li}_3(r_0)], \tag{22}$$

where

$$r_0 = \frac{\varepsilon_0^{Si} - 1}{\varepsilon_0^{Si} + 1} \approx 0.84. \tag{23}$$

Equation (22) demonstrates an abrupt change of the Casimir free energy in the transition point. In the high-temperature limit

$$k_B T \gg k_B T_{\mathrm{eff}} = \frac{\hbar c}{2a} \tag{24}$$

(at room temperature of $T = 300$ K this corresponds to separations $a > 5$ μm) the relative change of the free energy in accordance with (22) achieves 24%. Thus, in the point of phase transition the Casimir free energy and, as a consequence, the Casimir force undergo an abrupt change although the doping concentration and resistivity of the plate are both changing continuously. It follows that the reflection amplitudes of real electromagnetic waves on the plate cannot feel the phase transition that occurs with the increase of doping concentration and, thus, do not contain information on the respective change of the Casimir free energy in accordance with equation (22).

5. Problems with polar dielectrics

In the above, we have considered the dielectric permittivities in the form of (4). This form is commonly used for the description of electronic polarization which is inherent to all dielectrics. The respective oscillator frequencies belong to the ultraviolet spectrum. Some dielectrics, however, contain different ions (the typical examples are, for instance, SiO_2 and Al_2O_3). These dielectrics possess *ionic polarization*. Their dielectric permittivity can be also presented in the form of (4) but with oscillator frequencies belonging to the infrared spectrum. In both cases molecules do not possess intrinsic dipole moments, but only induced dipole moments due to the influence of the fluctuating electromagnetic field. One more type of
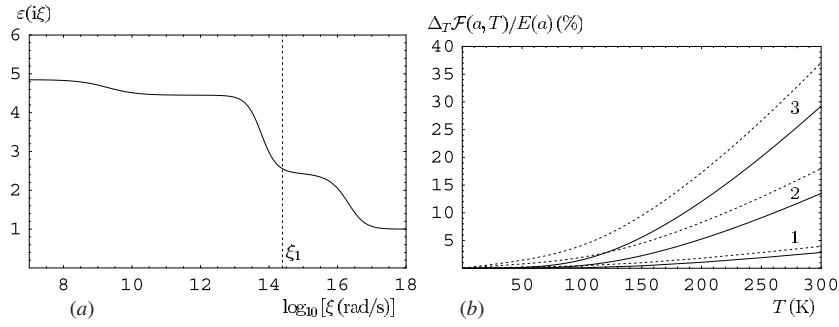
Figure 4. (a) Dielectric permittivity of mica along the imaginary frequency axis. The dashed line indicates the first Matsubara frequency at $T = 300$ K. (b) The relative thermal correction to the Casimir energy of mica plates as a function of temperature at separations $a = 100$ nm (lines labeled 1), $a = 500$ nm (lines labeled 2) and $a = 1$ μm (lines labeled 3). Solid lines are computed by taking into account the electronic and ionic polarization, whereas dashed lines take into account the orientation polarization as well.

dielectrics is the so-called *polar dielectrics* whose molecules possess intrinsic dipole moments which are oriented in the external electromagnetic field. In general, the dielectric permittivity of a dielectric with all three types of polarization along the imaginary frequency axis can be represented in the form [28]

$$\varepsilon(i\xi) = 1 + \frac{f_{\text{UV}}}{\omega_{\text{UV}}^2 + \xi^2} + \frac{f_{\text{IR}}}{\omega_{\text{IR}}^2 + \xi^2} + \frac{d}{1 + \xi\tau_D}. \tag{25}$$

Here, we have included for simplicity only one oscillator term describing the electronic polarization and one oscillator term describing the ionic polarization (the Ninham–Parsegian model). The last term on the right-hand side of (25) with the temperature-dependent parameters d and τ_D is the so-called Debye term which describes the orientation polarization. Typical values of $1/\tau_D$ belong to the microwave region of the spectrum.

Let us consider mica as an example of dielectric which possesses all the three types of polarization. The dielectric permittivity of mica along the imaginary frequency axis is plotted in figure 4(a). It corresponds to the following values of the parameters in (25): $\omega_{\text{UV}} = 10.33$ eV^2, $f_{\text{UV}} = 157.93$ eV^2, $\omega_{\text{IR}} = 3.95 \times 10^{-2}$ eV, $f_{\text{UV}} = 3.12 \times 10^{-3}$ eV^2 and, at room temperature, $\tau_D = 5 \times 10^{-8}$ s, $d = 0.4$ [28]. As is seen in figure 4(a), there are the three horizontal steps on the functional dependence of $\varepsilon(i\xi)$ on $\log_{10}\xi$ due to the three types of polarization. The step due to the electronic polarization is in the frequency region around 10^{15} rad s^{-1}. Being extrapolated to zero frequency, this step would lead to $\varepsilon_0^e = 2.45$. The step due to both electronic and ionic polarization is in the frequency region of order 10^{11}–10^{12} rad s^{-1}. The extrapolation of this step to zero frequency leads to $\varepsilon_0^{ei} = 4.45$. Finally, there is the third step at frequencies below 10^8 rad s^{-1} due to the electronic, ionic and orientation polarization. As a result, the static dielectric permittivity of mica due to all three types of polarization is equal to $\varepsilon_0^p = 4.85$.

At separations below 1 μm the Casimir energy at zero temperature, $E(a)$, is mostly determined by the electronic polarization. It is instructive to compare the relative magnitude of the thermal correction $\Delta_T\mathcal{F}(a, T)$ in (11) calculated with account of different types of polarization. Thus for Si, which possesses the electronic polarization only, $\Delta_T\mathcal{F}(a, T)/E(a) = 1.45\%$ at $T = 300$ K, $a = 500$ nm. If we disregard both ionic and orientation polarizations of mica and take into account only its electronic polarization, the

relative thermal correction is $\Delta_T \mathcal{F}(a, T)/E(a) = 1.25\%$ at the same T and a. Thus, the role of the electronic polarization of Si and mica is in fairly good agreement. However, in mica the ionic and orientation polarizations are also present. In figure 4(b) we plot the relative thermal correction, $\Delta_T \mathcal{F}(a, T)/E(a)$, for mica versus temperature at separations $a = 100$ nm (solid and dashed lines labeled 1), $a = 500$ nm (lines labeled 2) and $a = 1$ μm (lines labeled 3). All solid lines are computed taking the electronic and ionic polarization into account, i.e., using the dielectric permittivity with $\varepsilon_0^{ei} = 4.45$. The dashed lines are computed by using the complete dielectric permittivity (25), i.e., with account of the orientation polarization also. For simplicity the room temperature values of d and τ_D are used. As is seen in figure 4(b) (solid line 2), at $T = 300$ K the relative thermal correction achieves 13.5% (to compare with 1.25% found above with account of the electronic polarization only). Thus, the account of ionic polarization leads to a marked increase of the relative thermal correction.

In figure 4(b) it is seen also that the role of the orientation polarization increases with the increase of separation distance. Thus, at $a = 100$ nm, $T = 300$ K the account of orientation polarization leads to a 1% increase of the relative thermal correction, but at $a = 1$ μm to an 8% increase. We emphasize that the Debye term in dielectric permittivity (25) leads to problems in the Lifshitz theory. This term influences only the zero-frequency contribution to the Casimir free energy (1). As a result, the thermal correction with account of the orientation polarization is given by

$$\Delta_T \mathcal{F}^{(p)}(a, T) = \Delta_T \mathcal{F}(a, T) - \frac{k_B T}{16\pi a^2} \left[\mathrm{Li}_3(r_{0,p}^2) - \mathrm{Li}_3(r_{0,ei}^2) \right]. \qquad (26)$$

Here, $\Delta_T \mathcal{F}(a, T)$ is the thermal correction due to the electronic and ionic polarizations only and

$$r_{0,p} = \frac{\varepsilon_0^p - 1}{\varepsilon_0^p + 1}, \qquad r_{0,ei} = \frac{\varepsilon_0^{ei} - 1}{\varepsilon_0^{ei} + 1}. \qquad (27)$$

Note that $r_{0,p}$ depends on the temperature through the parameter d in (25). At temperatures of about $T = 300$ K (26) contains a contribution being approximately linear in the temperature. As to the first term on the right-hand side of (26), $\Delta_T \mathcal{F}(a, T)$, it has a standard form considered in [16, 17]. In [29] it was questioned whether or not the Debye term should be included in the model of dielectric response used in the Lifshitz theory. According to [29], the inclusion of the orientation degrees of freedom that come into play at very low frequencies much below the first Matsubara frequency is not justified. This problem calls for further investigation.

6. Conclusions and discussion

In the above, we have justified the rule that for a wide range of materials having zero conductivity at zero temperature (so-called *true dielectrics*) the conductivity arising at nonzero temperature must be disregarded in the calculation of the Casimir force using the Lifshitz theory. These materials include not only simple insulators, but also intrinsic semiconductors, Mott–Hubbard dielectrics and doped semiconductors with doping concentration below critical. We have proved that for all these materials the violation of this rule leads to a violation of the Nernst heat theorem for the Casimir entropy, so that the Lifshitz theory becomes thermodynamically inconsistent. Even more, the inclusion of conductivity properties of Si plate with doping concentration below the critical one into the model of dielectric response was shown to be inconsistent with the data of the recent experiment on the modulation of the Casimir force with laser pulses [10]. Thus, the proposed rule is not only warranted theoretically, but it has already obtained experimental confirmation. This is a problem of great concern for the Lifshitz theory because the inclusion of a negligible or relatively small

conductivity, arising in dielectrics at nonzero temperature, must not lead to theoretical results significantly different of those obtained under the neglect of this conductivity. What is more, one could expect that the theoretical results obtained with included conductivity are more exact. However, in reality these results are found to be simply invalid as being in contradiction with thermodynamics and inconsistent with the experimental data. Recently the modification of the Lifshitz theory of atom–wall interaction in the high-temperature limit was suggested [30] in the presence of spatial dispersion. The obtained interaction potential recovers the limiting cases of dielectrics and ideal conductors with account of low and high density of charge carriers, respectively. The proposed modification, however, was shown [31] to violate the Nernst theorem for a wide range of dielectrics and to be inconsistent with measurement data of experiment [10] at a 70% confidence level.

We have also considered the insulator–metal transition and demonstrated that in the transition point the Casimir free energy and force undergo an abrupt change. This may happen in an abrupt phase transition from one crystal structure to another one or, alternatively, with a continuous increase of doping concentration. In the latter case the doping concentration and resistivity are both continuous at room temperature in the point of phase transition. From this it follows that the reflection amplitudes of real electromagnetic waves do not contain information about the anomalous behavior of the Casimir force in the transition point.

One more problem occurs when applying the Lifshitz theory to polar dielectrics. We have shown that the account of orientation polarization results in large thermal correction at separations of about hundreds of nanometers that is a linear function of the temperature. Arguments are presented that this effect may be nonphysical.

To conclude, although there are serious problems in the application of the Lifshitz theory to real materials, a rule can be formulated allowing to avoid contradictions with thermodynamics and leading to theoretical results consistent with experiment.

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