PROBLEMS IN THE LIFSHITZ THEORY OF ATOM-WALL INTERACTION

G. L. KLIMCHITSKAYA*
Institute for Theoretical Physics, Leipzig University, D-04009, Leipzig, Germany
Galina.Klimchitskaya@itp.uni-leipzig.de

E. V. BLAGOV
Noncommercial Partnership “Scientific Instruments”, Moscow, Russia

V. M. MOSTEPANENKO†
Institute for Theoretical Physics, Leipzig University, D-04009, Leipzig, Germany

Received 30 October 2008
Revised 12 January 2009

Problems in the Lifshitz theory of atom-wall interaction arise when the dc conductivity of dielectric wall is included into the model of the dielectric response. We review the low-temperature behavior of the free energy and entropy of dispersion interaction for both dielectric and metallic walls. Consistency of the obtained results with thermodynamics and experimental data is analyzed. Recent attempts to include the screening effects and diffusion currents into the Lifshitz theory are considered. It is shown that this leads to the violation of the Nernst heat theorem for wide classes of wall materials. The physical reasons for the emergence of thermodynamic and experimental inconsistencies are elucidated.

Keywords: Casimir-Polder force; screening effects; Nernst’s heat theorem.

PACS numbers: 12.20.-m, 34.35.+a, 78.20.Ci

1. Introduction

The Lifshitz theory describes dispersion interaction between an atom or a molecule and a cavity wall which is caused by quantum fluctuations of the electromagnetic field. At separations from a few angstroms to a few nanometers the interaction of an atom with a wall is of nonrelativistic character. In this separation region it is described by the nonretarded van der Waals potential. At larger separations the relativistic effects come into play. At separations of about 1 μm the atom-wall interaction is described by the Casimir-Polder potential. The dispersion interaction

*On leave from North-West Technical University, St.Petersburg, Russia
†On leave from Noncommercial Partnership “Scientific Instruments”, Moscow, Russia
of atoms and molecules with walls made of different materials plays important role in physical, chemical and biological processes. During the last few years special attention was attracted to the role of atom-wall interaction in Bose-Einstein condensation and quantum reflection (see, e.g., Refs. 2–6 and references therein). In the framework of the Lifshitz theory material properties of a wall are described by the frequency-dependent dielectric permittivity and the properties of an atom by the atomic dynamic polarizability.

It is well known that the Lifshitz theory faces problems when the drift current of conduction electrons is taken into account in the model of the dielectric response (see the review in Ref. 7). These problems, connected with the violation of the third law of thermodynamics (the Nernst heat theorem) and contradictions between the theoretical predictions and experimental data, where mostly discussed in the case of two material plates. Here, we consider the complicated problems arising in the Lifshitz theory of atom-wall interaction which are connected with the description of free charge carriers in the wall material. In Sec. 2 we review known results for the Casimir-Polder free energy and entropy of atom-wall interaction in the limit of low temperatures. We show that for metallic walls theory is thermodynamically consistent, whereas for dielectric walls it is consistent with thermodynamics only if the dc conductivity of wall material is neglected in the model of the dielectric response. The physical reasons explaining why the difficulties with thermodynamics emerge are elucidated. In Sec. 3 the experimental test for the influence of charge carriers on the Casimir-Polder force is considered. Section 4 presents recent attempts to generalize the Lifshitz theory of the Casimir-Polder interaction through the inclusion of screening effects and diffusion currents. Here, we demonstrate that the obtained generalized reflection coefficients lead to contradiction between the Lifshitz theory and thermodynamics for a wide class of dielectric materials. The physical reasons why the screening effects are irrelevant to the van der Waals and Casimir-Polder interaction are explained. In Sec. 5 the reader will find our conclusions and discussion.

2. Asymptotic Behavior of the Casimir-Polder Free Energy and Entropy at Low Temperatures

The free energy of dispersion interaction of an atom (molecule) separated by a distance $a$ from a plate at temperature $T$ in thermal equilibrium with environment is given by the Lifshitz formula 2–4

$$F(a, T) = -\frac{k_B T}{8a^3} \sum_{l=0}^{\infty} \alpha(\omega_c \zeta_l) \int_{\zeta_l}^{\infty} dy e^{-y} \left[ (2y^2 - \zeta_l^2) r_{TM}(i\zeta_l, y) - \zeta_l^2 r_{TE}(i\zeta_l, y) \right].$$

(1)

Here, $\alpha(\omega)$ is the dynamic polarizability of an atom (molecule), $\zeta_l = \frac{4\pi k_B T a l}{\hbar c}$ [labels \(l = 0, 1, 2, \ldots\), $k_B$ is the Boltzmann constant, $\omega_c = c/(2a)$] are the dimensionless Matsubara frequencies, and the reflection coefficients for two independent polarizations of the electromagnetic field (transverse magnetic and transverse electric) are
Problems in the Lifshitz Theory of Atom-Wall Interaction

given by

\[ r_{TM}(i\zeta_l, y) = \frac{\varepsilon_l y - \sqrt{y^2 + \zeta_l^2(\varepsilon_l - 1)}}{\varepsilon_l y + \sqrt{y^2 + \zeta_l^2(\varepsilon_l - 1)}}, \quad r_{TE}(i\zeta_l, y) = \frac{y - \sqrt{y^2 + \zeta_l^2(\varepsilon_l - 1)}}{y + \sqrt{y^2 + \zeta_l^2(\varepsilon_l - 1)}}, \]

(2)

where \( \varepsilon_l \equiv \varepsilon(i\omega_c \zeta_l) \) is the dielectric permittivity of plate material along the imaginary frequency axis. The prime adds a multiple 1/2 to the term of (1) with \( l = 0 \).

For dielectrics with neglected dc conductivity the dielectric permittivity along the imaginary frequency axis is presented in the form

\[ \varepsilon_l = \frac{1}{\sum_j \frac{g_j}{\omega_j^2 + \omega^2_\zeta_l^2 + \gamma_j \omega_c \zeta_l}} \approx 1 + \sum_j \frac{g_j}{\omega_j^2 + \omega^2_\zeta_l^2}, \]

(3)

where \( \omega_j \neq 0 \) are the oscillator frequencies, \( g_j \) are the oscillator strengths and \( \gamma_j \) are the relaxation parameters. This representation assumes that the static permittivity of a dielectric material is finite:

\[ \varepsilon_0 = \varepsilon(0) = 1 + \sum_j \frac{g_j}{\omega_j^2} < \infty. \]

(4)

The atomic dynamic polarizability can be represented with sufficient precision using the single-oscillator model

\[ \alpha(i\omega_c \zeta_l) = \frac{\alpha(0)}{1 + \beta^2 \zeta_l^2}. \]

(5)

with a dimensionless constant \( \beta \). The asymptotic behavior of the free energy \( \mathcal{F} \) combined with the dielectric permittivity \( \varepsilon_0 \) at low temperatures was found in Ref. [12]. Under the condition \( \tau = 2\pi T/T_{\text{eff}} \ll 1 \), where the effective temperature is defined by \( k_B T_{\text{eff}} = \hbar \omega_c \), it holds

\[ \mathcal{F}(a, T) \approx E(a) - \frac{\hbar c \pi^3}{240a^4} \alpha(0) C(\varepsilon_0) \left( \frac{T}{T_{\text{eff}}} \right)^4. \]

(6)

Here, \( E(a) \) is the Casimir-Polder energy at zero temperature and \( C(\varepsilon_0) \) is the function which goes to zero when \( \varepsilon_0 \to 1 \) (see Ref. [12] for the explicit form of it). For commonly used dielectrics, such as SiO\(_2\) with \( \varepsilon_0 = 3.81 \) and Si with \( \varepsilon_0 = 11.67 \), \( C(\varepsilon_0) \) is equal to 2.70 and 6.33, respectively. From (6) the Casimir-Polder entropy is given by

\[ S(a, T) = -\frac{\partial \mathcal{F}(a, T)}{\partial T} \approx \frac{\pi^3 k_B}{30a^3} \alpha(0) C(\varepsilon_0) \left( \frac{T}{T_{\text{eff}}} \right)^3. \]

(7)

As is seen from this equation, the Casimir-Polder entropy goes to zero when \( T \) vanishes, i.e., the Lifshitz theory with the permittivity \( \varepsilon_0 \) satisfies the Nernst heat theorem.

The model of the dielectric response \( \varepsilon_0 \) does not take into account, however, that all dielectrics at nonzero temperature possess small but physically real dc conductivity. For dielectric materials conductivity vanishes with temperature exponentially
fast:

$$\sigma(i\omega_c, T) \sim \exp\left(-\frac{\Delta}{k_B T}\right) \rightarrow 0 \text{ when } T \rightarrow 0,$$

(8)

where the physical meaning of the coefficient $\Delta$ is different for different classes of dielectrics. The dc conductivity is usually taken into account by means of the Drude-like term

$$\tilde{\varepsilon}_l = \varepsilon_l + \frac{4\pi\sigma(i\omega_c, T)}{\omega_c \varepsilon_l},$$

(9)

where

$$\sigma(i\omega_c, T) = \frac{\sigma(0, T)}{1 + \frac{\omega_c \varepsilon_l}{\gamma}},$$

(10)

where $\sigma(0, T)$ is the dc conductivity and $\gamma$ is the relaxation parameter of free electrons.

The substitution of the permittivity (9) into the Lifshitz formula (1) leads to only negligible additions to all terms with $l \geq 1$. These additions exponentially decay to zero with vanishing temperature.\textsuperscript{16–18} However, the term with $l = 0$ is modified because according to (2) $\tilde{r}_{TM}(0, y) \equiv r_0 = (\varepsilon_0 - 1)/(\varepsilon_0 + 1)$ is replaced with $\tilde{r}_{TM}(0, y) = 1$. As a result, with dc conductivity included the free energy at low temperature is given by\textsuperscript{12}

$$\tilde{F}(a, T) \approx F(a, T) - k_B T 4a^3 (1 - r_0) \alpha(0),$$

(11)

where $F(a, T)$ is presented in Eq. (6). Then the entropy at zero temperature is obtained using the first equality in Eq. (7)

$$\tilde{S}(a, 0) = \frac{k_B}{4a^3}(1 - r_0) \alpha(0) > 0.$$

(12)

This is in violation of the third law of thermodynamics because the Casimir-Polder entropy at $T = 0$ depends on the parameters of the system, such as separation distance, static dielectric permittivity and static atomic polarizability. In Ref.\textsuperscript{12} the contradiction between the Lifshitz theory of atom-wall interaction with included dc conductivity of the wall and thermodynamics is explained by the violation of thermal equilibrium. The drift current of charge carriers $j = \sigma E$ incorporated in the permittivity (7) leads to Joule’s heating of the wall (Ohmic losses).\textsuperscript{19} Then to preserve the temperature constant, one should admit the existence of an unidirectional flux of heat from the wall to the heat bath.\textsuperscript{20} Such fluxes are excluded in the state of thermal equilibrium. In fact the drift current is irreversible process which goes with an increase of entropy and brings a system out of thermal equilibrium. Thus, it cannot be included in the Lifshitz theory formulated for equilibrium systems.

The low-temperature behavior of the Casimir-Polder free energy and entropy for an atom (molecule) near a metal wall was considered in Ref.\textsuperscript{6} Metal of the wall
was described by means of the plasma model

\[ \varepsilon_p^1 = 1 + \frac{\omega_p^2}{\omega_c^2}, \]  

(13)

where \( \omega_p = (4\pi e^2 n/m)^{1/2} \) is the plasma frequency, \( n \) is the density of charge carriers, \( e \) is the charge of an electron and \( m \) is its effective mass. Similar results can be also obtained using the Drude model for the description of the metal. The reason is that for metals not the TM reflection coefficient at \( \zeta_0 = 0 \), but the TE one leads to the discontinuity in the zero-frequency contribution to the Lifshitz formula. However, for an atom-wall interaction the TE reflection coefficient at zero frequency in Eq. (1) is multiplied by \( \zeta_0^2 = 0 \) and thus does not contribute to the result.

Under the conditions \( \tau \ll 1 \) and \( \delta_0/a \equiv c/(\omega_p) \ll 1 \) the leading terms of the asymptotic expressions for the Casimir-Polder free energy and entropy are given by

\[ F^p(a, T) \approx E^p(a) - \frac{\hbar c \pi^3}{360a^4} \alpha(0) \left( \frac{T}{T_{\text{eff}}} \right)^4, \]

\[ S^p(a, T) \approx \frac{\pi^3 k_B}{45a^3} \alpha(0) \left( \frac{T}{T_{\text{eff}}} \right)^3, \]

(14)

where \( E^p(a) \) is the energy of atom-wall interaction at \( T = 0 \) calculated using the plasma model. Note that the results (14) are the same as for an atom near an ideal metal plate. Small corrections to these results depending on atomic and material properties (\( \beta \) and \( \delta_0 \)) are obtained in Ref. [6]. For us it is only important that the entropy in Eq. (14) vanishes when \( T \to 0 \), i.e., in the case of a metallic wall the Nernst heat theorem is satisfied.

3. Experimental Test for the Influence of Charge Carriers

Important experimental test for the role of dc conductivity in the interaction of atoms with a dielectric wall was performed in Ref. [5]. This is the measurement of the thermal Casimir-Polder force through center-of-mass oscillations of the trapped Bose-Einstein condensate. In that experiment the dipole oscillations with the frequency \( \omega_0 \) were excited in a \(^{87}\text{Rb} \) Bose-Einstein condensate separated by a distance of a few micrometers from a fused-silica (SiO\(_2\)) wall. The Casimir-Polder force acting between a Rb atom and a wall changed the magnitude of the oscillation frequency making it equal to some \( \omega_z \). The fractional frequency difference \( \gamma_z = |\omega_0 - \omega_z|/\omega_0 \) was measured and compared with theory at an environment temperature \( T_E = 310 \text{K} \) and at different wall temperatures \( T_W = 310 \text{K} \) (thermal equilibrium) and \( T_W = 479 \text{K}, 605 \text{K} \) (out of thermal equilibrium).

In the original publication [5] the wall material was considered as a dielectric with finite static dielectric permittivity \( \varepsilon_0 = 3.81 \). Under this assumption, computations using the Lifshitz formula (1) and respective expression for situations out of thermal equilibrium [23] demonstrated a very good agreement between experiment and
theory at a 70% confidence level. However, as was discussed in Sec. 2, at nonzero temperature SiO$_2$ has nonzero conductivity which is ionic in nature and varies from $10^{-9}$ s$^{-1}$ to $10^2$ s$^{-1}$ depending on the concentration of alkali ions which are always present as trace constituents. In Ref. [24] the fractional frequency difference $\gamma_z$ was recalculated both in equilibrium and out of thermal equilibrium by taking into account a nonzero dc conductivity of fused silica in accordance to Eq. (9). It was shown that the inclusion of the dc conductivity leads to drastically different theoretical results both in thermal equilibrium and out of thermal equilibrium which are in disagreement with the measurement data.

In Fig. 1 the experimental data for $\gamma_z$ obtained in thermal equilibrium are shown as crosses at different separations. The arms of the crosses indicate the experimental errors determined individually at each data point at a 70% confidence level. The solid and dashed lines show the theoretical results computed with neglect and inclusion of the dc conductivity, respectively. Importantly, the obtained results with included dc conductivity do not depend on its magnitude, but only on the fact that it is nonzero. As is seen in Fig. 1, the first two experimental points are in clear disagreement with the dashed line taking into account the conductivity of fused silica. Similar conclusions are obtained in situations out of thermal equilibrium. In Fig. 2(a,b) the same information, as in Fig. 1, is provided for wall temperatures $T_W = 479$ K and 605 K, respectively. As is seen in Fig. 2, in nonequilibrium situations the disagreement between the experimental data shown as crosses and the theory taking into account the dc conductivity of a SiO$_2$ wall (the dashed lines) further widens. As is seen in Fig. 2(a), the three experimental points exclude the dashed line and the other two only touch it. In Fig. 2(b) all data points exclude the theoretical prediction incorporating the dc conductivity of a SiO$_2$ wall. The solid lines in Fig. 2(a,b) computed with the dc conductivity neglected are in a very good agreement with the measurement data. Thus, the inclusion of the dc conductivity of dielectric materials into the Lifshitz theory is not only in contradiction with

![Figure 1](image)

**Fig. 1.** Fractional frequency difference versus separation in thermal equilibrium with $T_W = T_E = 310$ K computed by neglecting (solid line) and including (dashed line) the conductivity of the wall. The experimental data are shown as crosses.
Problems in the Lifshitz Theory of Atom-Wall Interaction

7

thermodynamics (see Sec. 2), but is also experimentally inconsistent.

4. Attempts to Include the Screening Effects

Recently several attempts were undertaken\textsuperscript{8–10} to solve the problem of free charge carriers in the Lifshitz theory through the inclusion into consideration of screening effects and diffusion currents. Here, we discuss these attempts only in the case of atom-wall interaction (for the case of plate-plate interaction see Ref. 25). The consideration of the scattering problem with account of both the drift and diffusion currents of free charge carriers through use of the Boltzmann transport equation results in the modified reflection coefficients for the TM and TE modes of the electromagnetic field.\textsuperscript{9}

The modified TM reflection coefficient is given by

\[
r_{\text{TM}}^{\text{mod}}(\zeta_l, y) = \frac{\tilde{\epsilon}_l y - [y^2 + (\tilde{\epsilon}_l - 1)\zeta_l^2]^{1/2} - (y^2 - \zeta_l^2)(\tilde{\epsilon}_l - \epsilon_l)\tilde{\eta}_l^{-1}\epsilon_l^{-1}}{\tilde{\epsilon}_l y + [y^2 + (\tilde{\epsilon}_l - 1)\zeta_l^2]^{1/2} + (y^2 - \zeta_l^2)(\tilde{\epsilon}_l - \epsilon_l)\tilde{\eta}_l^{-1}\epsilon_l^{-1}},
\]

where \(\epsilon_l, \tilde{\epsilon}_l\) are defined in Eqs. (3), (9) and

\[
\tilde{\eta}_l = \left[ y^2 - \zeta_l^2 + \kappa_a^2 \frac{\epsilon_0 \epsilon_l}{\epsilon_l (\tilde{\epsilon}_l - \epsilon_l)} \right]^{1/2}, \quad \kappa_a = 2\kappa.
\]

The parameter \(\kappa\) in Eq. (16) is the inverse of the screening length. If the density of charge carriers \(n\) is sufficiently small, so that they are described by the classical Maxwell-Boltzmann statistics, one gets the Debye-Hückel screening length\textsuperscript{26}

\[
R_{\text{DH}} = \frac{1}{\kappa_{\text{DH}}} = \sqrt{\frac{\epsilon_0 k_B T}{4\pi e^2 n}}
\]

Assuming high density of charge carriers obeying the Fermi-Dirac statistics, one arrives at the Thomas-Fermi screening length\textsuperscript{26}

\[
R_{\text{TF}} = \frac{1}{\kappa_{\text{TF}}} = \sqrt{\frac{\epsilon_0 E_F}{6\pi e^2 n}}.
\]
where \( E_F = \hbar \omega_p \) is the Fermi energy. As to the modified TE reflection coefficient, \( r_{\text{TE}}^{\text{mod}}(i\zeta_l, y) \), it is given by the standard Eq. (2) where the permittivity \( \varepsilon_l \) is replaced with \( \tilde{\varepsilon}_l \).

At zero Matsubara frequency the modified reflection coefficients are given by

\[
\begin{align*}
\r_{\text{TM}}^{\text{mod}}(0, y) &= \frac{\varepsilon_0 \sqrt{y^2 + \kappa_l^2} - y}{\varepsilon_0 \sqrt{y^2 + \kappa_l^2} + y}, \\
\r_{\text{TE}}^{\text{mod}}(0, y) &= 0.
\end{align*}
\]

(19)

The coefficient \( \r_{\text{TM}}^{\text{mod}}(0, y) \) from Eq. (19) was first obtained in Ref. 8, where only the static case and atom-wall interaction at large separations were considered. In so doing, all other reflection coefficients were assumed to be unmodified. The reflection coefficients (19) were also reobtained in Ref. 10 using the phenomenological nonlocal approach. At all nonzero Matsubara frequencies the coefficients in Refs. 9 and 10 differ between themselves and from unmodified coefficients only slightly. As shown in Ref. 25, in application to the case of two parallel plates the substitution of the modified reflection coefficients into the Lifshitz formula results in violation of the Nernst heat theorem for a wide class of materials and is excluded experimentally.

Here, we perform the thermodynamic test of the modified reflection coefficients for atom-wall interaction at all Matsubara frequencies (in Ref. 12 only the approach of Ref. 8 was tested where the reflection coefficients at all nonzero Matsubara frequencies remained unmodified).

References 8–10 substitute the modified reflection coefficients into the standard Lifshitz formula (1) for the free energy of dispersion interaction. We start with the case of dielectric wall and find the asymptotic behavior of the free energy at low temperature. For this purpose we introduce the small parameter

\[
\beta_l = \frac{4\pi\sigma(0, T)}{\omega_c \zeta_l} \ll 1, \quad l \geq 1,
\]

(20)

which goes to zero due to Eq. (8) when temperature vanishes. Then we expand the modified reflection coefficients \( r_{\text{TM,TE}}^{\text{mod}}(i\zeta_l, y) \) with \( l \geq 1 \) in powers of this parameter

\[
\begin{align*}
\r_{\text{TM}}^{\text{mod}}(i\zeta_l, y) &= \r_{\text{TM}}(i\zeta_l, y) + \beta_l \frac{\varepsilon_l y[2y^2 + (\varepsilon_l - 2)\zeta_l^2]}{\sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2}[\varepsilon_l y + \sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2}]} + O(\beta_l^2), \\
\r_{\text{TE}}^{\text{mod}}(i\zeta_l, y) &= \r_{\text{TE}}(i\zeta_l, y) + \beta_l \frac{y[y - \sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2}]}{\sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2}[y + \sqrt{y^2 + (\varepsilon_l - 1)\zeta_l^2}]} + O(\beta_l^2).
\end{align*}
\]

(21)

Here, the reflection coefficients \( \r_{\text{TM,TE}} \) are defined by Eq. (2) with the dielectric permittivity of core electrons (3). The Casimir–Polder free energy \( \mathcal{F}(a, T) \) calculated with these coefficients vanishes with temperature as \( \sim (T/T_{\text{eff}})^4 \) according to Eq. (6).

Substituting (21) into the free energy of atom-wall interaction (1) one obtains

\[
\mathcal{F}^{\text{mod}}(a, T) = \mathcal{F}(a, T) - \frac{k_B T a_0(0)}{8a^3} \left[ \int_0^\infty y^2 dy \r_{\text{TM}}^{\text{mod}}(0, y)e^{-y} - 2r_0 + Q_1(T) \right],
\]

(22)
where \( Q_1(T) \) vanishes exponentially when \( T \to 0 \). Calculating the negative derivative of both sides of (22) with respect to \( T \), we arrive at

\[
S^{\text{mod}}(a, T) = S(a, T) + \frac{k_B \alpha(0)}{8a^3} \left[ \int_0^\infty y^2 dy r_{\text{TM}}^{\text{mod}}(0, y)e^{-y} - 2r_0 \right] + \varepsilon_0 T \frac{\partial \kappa^2}{\partial T} \int_0^\infty dy \frac{y^3 e^{-y}}{\sqrt{y^2 + \kappa_a^2 (\varepsilon_0 \sqrt{y^2 + \kappa_a^2} + y)^2}} + Q_1(T) + T Q'_1(T),
\]

where \( S(a, T) \) is defined in Eq. (7) and \( \kappa_a = 2a \kappa_{\text{DH}} \).

Now we are in a position to perform the thermodynamic test for the approaches taking the screening effects into account. The dc conductivity can be represented as

\[
\sigma(0, T) = \mu(T) |e| n(T),
\]

where \( \mu(T) \) is the mobility of charge carriers. For dielectric material with exponentially decaying \( n(T) \) in the limit of low \( T \), \( r_{\text{TM}}^{\text{mod}}(0, y) \to r_0 \) and all terms on the right-hand side of Eq. (23) added to \( S(a, T) \) go to zero when \( T \to 0 \).

As a result, \( S^{\text{mod}}(a, T) \) goes to zero when \( T \) vanishes, following the same law, \( \sim (T/T_{\text{eff}})^3 \), as \( S(a, T) \), and the Nernst heat theorem is satisfied. However, for many dielectric materials (such as semiconductors doped below critical dopant concentration, semimetals of dielectric type, some amorphous semiconductors or solids with ionic conductivity) \( n(T) \) does not go to zero in the limit \( T \to 0 \). For such materials the dc conductivity \( \sigma(0, T) \) goes to zero exponentially fast (as for all dielectrics) due to the vanishing mobility \( \mu(T) \) in Eq. (24). For all dielectric materials with nonvanishing \( n \) it holds \( r_{\text{TM}}^{\text{mod}}(0, y) \to 1 \) when \( T \) and \( \mu(T) \) simultaneously vanish. This is because \( \kappa_{\text{DH}} \to \infty \) when \( T \to 0 \) in accordance with Eq. (17). In this case Eq. (23) results in

\[
S^{\text{mod}}(a, 0) = \frac{k_B}{4a^3} (1 - r_0) \alpha(0) > 0,
\]

i.e., the Nernst heat theorem is violated in the same way as in the standard Lifshitz theory with included dc conductivity [see Eq. (12)]. Mathematically, the reason of violation is the discontinuity of the TM reflection coefficient as a function of \( \xi \) and \( T \) at the origin of the \((\xi, T)\)-plane [22]. Note that claim of Ref. [10] that the approach taking the screening effects into account is consistent with thermodynamics is incorrect. As shown in Refs. [25, 28], this claim is based on misinterpretation of relevant physical quantities. Similar claim made in Ref. [29] is also incorrect. The proof of the validity of the Nernst theorem given in Ref. [29] uses the condition that \( n \to 0 \) when \( T \) vanishes. Thus, this proof simply ignores wide classes of dielectric materials for which this is not so and the Nernst theorem is violated.

The physical reason for the inconsistency with thermodynamics discussed above is the violation of the applicability conditions of the Lifshitz theory. The drift and diffusion currents described by the Boltzmann transport equation are irreversible processes out of thermal equilibrium which go with an increase of the entropy. As
to the Lifshitz theory, it is formulated under the condition of thermal equilibrium and describes equilibrium systems. Because of this, the substitution of the modified reflection coefficients into the standard Lifshitz formula \( (1) \) leads to thermodynamic puzzles.

In the end of this section we consider atom-wall interaction in the case of metallic walls when the screening effects are taken into account. In this case one should use \( \kappa = \kappa_{\text{TF}} \). For metals, \( \kappa_a = 2\pi \kappa_{\text{TF}} \) is very large and the inverse quantity \( \beta_a \equiv \frac{1}{\kappa_a} \ll 1 \) can be used as a small parameter. The expansion of the TM reflection coefficient \( (15) \) in powers of \( \beta_a \) takes the form

\[
r_{\text{TM}}^\text{mod}(i\zeta, y) = \tilde{r}_{\text{TM}}(i\zeta, y) - 2\beta_a Z_l + O(\beta_a^2), \tag{26}
\]

where \( Z_l \equiv \sqrt{\tilde{\epsilon}_l(\tilde{\epsilon}_l - \epsilon_l)} \frac{y(y^2 - \zeta_l^2)}{\sqrt{y^2 + (\tilde{\epsilon}_l - 1)\zeta_l^2}^2} \).

After the substitution of Eq. (26) and the expression for \( r_{\text{TE}}(i\zeta, y) \) (the latter coincides with the known expression for the TE reflection coefficient \( (30) \) obtained using the Drude model) into Eq. (1), one obtains

\[
F_{\text{mod}}(a, T) = F_p(a, T) + \beta_a F(\beta)(a, T), \tag{27}
\]

where \( F_p(a, T) \) is defined in Eq. (14) and the quantity \( F(\beta)(a, T) \) originates from the second contribution on the right-hand side of Eq. (26). It is easily seen that at low \( T \) the quantity \( F(\beta)(a, T) \) behaves as \( F(\beta)(a, T) = E(\beta)(a) + O(T^5/T_{\text{eff}}^5) \). Calculating the negative derivative with respect to temperature from both sides of Eq. (27), we arrive to the equality \( S_{\text{mod}}(a, 0) = 0 \), i.e., in the case of metallic walls the Nernst heat theorem is satisfied. This result is preserved if metal wall is described by means of the Drude model.

5. Conclusions and Discussion

In the foregoing we have discussed problems in the Lifshitz theory of atom-wall interaction connected with the description of free charge carriers in wall material. It was shown that in the case of metallic walls this does not create any problem. As to dielectric walls, thermodynamically and experimentally consistent results are obtained when the dc conductivity of wall material is neglected. The inclusion of the dc conductivity into the model of dielectric response results in the violation of the Nernst heat theorem and in contradictions with experimental data. Similar situation also holds in recently proposed theoretical approaches attempting to include in the Lifshitz theory the screening effects and diffusion currents. For metallic walls this does not create problems, but leads to contradictions with thermodynamics for wide classes of dielectrics. Consistent theoretical description of atom-wall interaction in the case of dielectric walls uses the rule that the dc conductivity of dielectric material should be neglected\( (24) \).
This rule should be considered as a phenomenological one, but it can be justified in terms of most basic physical concepts on the subject. The point is that the physical phenomenon of dispersion forces occurs in thermal equilibrium and is caused by the fluctuating electromagnetic field. The latter cannot transmit energy in only one direction from the field to charge carriers, heat the wall material and create in homogeneous media the nonhomogeneous concentrations of charges resulting in the screening and diffusion effects. All these phenomena are of irreversible character, lead to an increase of the entropy and can occur in external electric field. Thus, we get the conclusion that there is a fundamental difference between the fluctuating electromagnetic field (including its “static component”) and external electric field. The discussed above problems in both the standard formulation of the Lifshitz theory of atom-wall interaction and its generalization including the screening effects arise when the properties of external field are attributed to the fluctuating field in an unjustified way. Final clarification of this issue is expected in near future.

Acknowledgments

G.L.K. and V.M.M. are grateful to the Center of Theoretical Studies and the Institute for Theoretical Physics, Leipzig University, for their kind hospitality. They were partially supported by Deutsche Forschungsgemeinschaft, Grant No. 436 RUS 113/789/0–4.

References

1. V. A. Parsegian, *Van der Waals Forces: A Handbook for Biologists, Chemists, Engineers, and Physicists* (Cambridge University Press, Cambridge, 2005).
2. J. F. Babb, G. L. Klimchitskaya and V. M. Mostepanenko, *Phys. Rev. A* **70**, 042901 (2004).
3. M. Antezza, L. P. Pitaevskii and S. Stringari, *Phys. Rev. A* **70**, 053619 (2004).
4. A. O. Caride, G. L. Klimchitskaya, V. M. Mostepanenko and S. I. Zanette, *Phys. Rev. A* **71**, 042901 (2005).
5. J. M. Obrecht, R. J. Wild, M. Antezza, L. P. Pitaevskii, S. Stringari and E. A. Cornell, *Phys. Rev. Lett.*, **98**, 063201 (2007).
6. V. B. Bezerra, G. L. Klimchitskaya, V. M. Mostepanenko and C. Romero, *Phys. Rev. A* **78**, 042901 (2008).
7. G. L. Klimchitskaya and V. M. Mostepanenko, *Contemp. Phys.* **47**, 131 (2006).
8. L. P. Pitaevskii, *Phys. Rev. Lett.* **101**, 163202 (2008).
9. D. A. R. Dalvit and S. K. Lamoreaux, *Phys. Rev. Lett.* **101**, 163203 (2008).
10. V. B. Svetovoy, *Phys. Rev. Lett.* **101**, 163603 (2008).
11. E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics*, Pt.II (Pergamon, Oxford, 1984).
12. G. L. Klimchitskaya, U. Mohideen and V. M. Mostepanenko, *J. Phys. A: Math. Theor.* **41**, 432001 (2008).
13. B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors. Solid State Series*, v.45 (Springer, Berlin, 1984).
14. G. L. Klimchitskaya and B. Geyer, *J. Phys. A: Math. Theor.* **41**, 164032 (2008).
15. E. D. Palik (ed.), *Handbook of Optical Constants of Solids* (Academic, New York, 1985).
16. B. Geyer, G. L. Klimchitskaya and V. M. Mostepanenko, *Phys. Rev. D* **72**, 085009 (2005).
17. B. Geyer, G. L. Klimchitskaya and V. M. Mostepanenko, *Int. J. Mod. Phys. A* **21**, 5007 (2006).
18. B. Geyer, G. L. Klimchitskaya and V. M. Mostepanenko, *Ann. Phys. (N.Y.)* **323**, 291 (2008).
19. B. Geyer, G. L. Klimchitskaya and V. M. Mostepanenko, *Phys. Rev. A* **67**, 062102 (2003).
20. V. V. Bryksin and P. M. Petrov, *Phys. Solid State* **50**, 229 (2008).
21. J. S. Høye, I. Brevik, J. B. Aarseth and K. A. Milton, *J. Phys. A: Math. Gen.* **39**, 6031 (2006).
22. V. B. Bezerra, R. S. Decca, E. Fischbach, B. Geyer, G. L. Klimchitskaya, D. E. Krause, D. López, V. M. Mostepanenko and C. Romero, *Phys. Rev. E* **73**, 028101 (2006).
23. M. Antezza, L. P. Pitaevskii and S. Stringari, *Phys. Rev. Lett.* **95**, 113202 (2005).
24. G. L. Klimchitskaya and V. M. Mostepanenko, *J. Phys. A: Math. Theor.* **41**, 312002 (2008).
25. V. M. Mostepanenko, R. S. Decca, E. Fischbach, B. Geyer, G. L. Klimchitskaya, D. E. Krause, D. López and U. Mohideen, *Int. J. Mod. Phys. A* **24**, this issue.
26. J.-N. Chazalviel, *Coulomb Screening of Mobile Charges: Applications to Material Science, Chemistry and Biology* (Birkhauser, Boston, 1999).
27. F. Intravaia and C. Henkel, *J. Phys. A: Math. Theor.* **41**, 164018 (2008).
28. G. L. Klimchitskaya, U. Mohideen and V. M. Mostepanenko, [arXiv:0810.3247](http://arxiv.org/abs/0810.3247)
29. D. A. R. Dalvit and S. K. Lamoreaux, [arXiv:0812.0557](http://arxiv.org/abs/0812.0557)
30. V. B. Bezerra, G. L. Klimchitskaya, V. M. Mostepanenko and C. Romero, *Phys. Rev. A* **69**, 022119 (2004).