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Semi-Classical Electrodynamics and the Casimir Effect

Mathias Boström [1,2,*], Ayda Gholamhosseinian [3], Subhojit Pal [1], Yang Li [4,5] and Iver Brevik [6,*]

[1] Centre of Excellence ENSEMBLE3 Sp. z o. o., Wolczynska Str. 133, 01-919 Warsaw, Poland; subhojit18@iiserb.ac.in
[2] Chemical and Biological Systems Simulation Lab, Centre of New Technologies, University of Warsaw, Banacha 2C, 02-097 Warsaw, Poland
[3] School of Physics and Materials Science, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran; ayda.gholamhosseinian@mail.um.ac.ir
[4] School of Physics and Materials Science, Nanchang University, Nanchang 330031, China; leon@ncu.edu.cn
[5] Institute of Space Science and Technology, Nanchang University, Nanchang 330031, China
[6] Department of Energy and Process Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway
* Correspondence: mathias.bostrom@ensemble3.eu (M.B.); iver.h.brevik@ntnu.no (I.B.)

Abstract: From the late 1960s onwards, the groups of Barry Ninham and Adrian Parsegian, and their many collaborators, made a number of essential contributions to theory and experiment of intermolecular forces. In particular, they explored the semi-classical theory: Maxwell's equations and Planck quantization of light leads to Lifshitz and Casimir interactions. We discuss some selected thought-provoking results from Ninham and his group. Some of the results have been conceived as controversial but, we would say, never uninteresting.

Keywords: Lifshitz forces; Casimir effect; semi-classical electrodynamics

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1. Introduction

Since the prediction of the Casimir effect in 1948, and its experimental confirmation in the period after that, there has been a significant interest in studying the forces caused by fluctuations both theoretically and experimentally [1,2]. Before reviewing some contributions to Casimir physics from semi-classical electrodynamics theory, that is Maxwell's equations and Planck quantization of light leading to Lifshitz and Casimir interactions, with particular emphasis on the paper by Barry Ninham and collaborators, we first present some historical reflections. The history of intermolecular forces actually goes back to the early history of science. Thomas Young notably wrote a paper on molecular forces in 1805 [3,4]. Young deduced that they had to obey $1/r^6$-power-law, where r is the average distance between molecules. Reverend Pam Challis of Trinity College, in a major address to the British Association 1836 [5], reviewed the state of molecular forces between colloidal particles, suggested interferometry for direct measurements, quoting Augustin-Jean Fresnel, and referred to the subject as "this the highest Department of Science" for which he coined the term Mathematical Physics. The renowned article by James Clerk Maxwell in the nineth edition of Encyclopaedia Britannica [6] discussed capillary action and molecular forces, updated by Lord Rayleigh in the 11th edition [7]. Roger Boscovich (Ruđer Bošković), a Croatian Jesuit Priest based in Rome after whom the Ruđer Bošković Institute in Zagreb is named, developed a system of the world essentially inventing statistical mechanics (his book [8] appeared around 1600). To do so, Boscovich needed a molecular potential. His effective potential oscillated with the period a molecular diameter tailing off into a gravitational $1/r^2$. The basis of the study of intermolecular forces was laid by Johannes Diderik van der Waals in 1873 [9] (see English translation in Ref. [10]). He clarified the concept of interparticle forces and how molecules interact. Quantum fluctuations create intermolecular forces that exist throughout macroscopic bodies. At the molecular separations of about a few nanometres or less, these interactions causing the attraction and repulsion between molecules, are the familiar van der Waals forces.

As discussed by Boris Derjaguin, Irina Abrikossova, and Evgeny Lifshitz in their 1956 review paper [11], the correct understanding of the nature of molecular forces was initially proposed by Peter (Pyotr) N. Lebedev, back in 1894 [11,12]: "There exist intermolecular forces whose origin is closely connected with radiation processes." In general, it is necessary to understand van der Waals forces and understand their importance compared to other molecular forces.

Fundamental and applied research on molecular forces continued until Fritz London proposed the general theory of molecular forces in 1930 [13]. This theoretically improved the understanding of molecular dispersion forces, and contributed to the interpretation of van der Waals forces and other molecular forces. Also, the significant contributions of Lifshitz should be addressed. In 1955, Lifshitz explained how the oscillating charge distribution in molecules leads to the creation of attractive forces [14]. These explanations contribute to a deeper understanding of molecular forces and their role in various phenomena.

Ever since Derjaguin and Abrikossova [11] performed their force measurements, there has been a strong focus on the phenomena The first set of experiments, notably measuring interactions between quartz and metal plates, studied only the so-called retarded region. Experiments of David Tabor and Ralph Winterton [15] and subsequently of Jacob Israelachvili and Tabor [16,17] fitted the measured force to a power law function of $1/L^p$ (where L is the distance), where p varied from non-retarded ($p = 3$) to fully retarded ($p = 4$) value. In these early experiments, a gradual transition was observed from non-retarded to retarded interaction, as the distance between the surfaces increased from around 12 nm upto 130 nm [16]. Surface force measurements [11,15–18] and theoretical clarifications and extensions of the Lifshitz formula [19–23] to include, for example, magnetic [24] and conducting particles [25,26], and liquids between unequal surfaces, were pioneered in the 1970s by the group of Ninham, Israelachvili, and their collaborators at the Department of Applied Mathematics in the Australian National University.

According to the fundamental theory, the Lifshitz force can also be repulsive, which is an interesting feature that has attracted quite some of attention [19,27,28]. Charles Anderson and Edward Sabiski demonstrated this phenomenon in their research on liquid helium films on smooth surfaces of calcium fluorite (CaF_2), among other similar molecularly smooth surfaces [29]. The thickness of the films in the experiment ranged from 10 Å to 200 Å, and could be measured with an accuracy of a few percent in most cases. Several past publications by Ninham have explored the history of intermolecular forces in more detail. The book by Ninham and Pierandrea Lo Nostro [30] is of a particular interest.

We focus first on reviewing a study that our close and distinguished collaborator Barry Ninham wrote in 1970 together with Adrian V. Parsegian and George H. Weiss [21]. The reason to highlight this paper is that it seems to us it is not recognized well enough in the field. The theories of intermolecular dispersion forces have occupied such a vast literature that one would suspect quite little should remain to be said. However, even lately, new applications of the fundamental theory have arisen. We firstly address the semi-classical theory itself, and then briefly discuss our contribution to the theory of Casimir interaction between real metal plates at high temperatures/large separations. A controversial, as well as especially intriguing, idea is briefly explored in the current paper, highlighting that the high-temperature Casimir effect might have a role even in nuclear physics [31]. To be more specific: it was shown in an unpublished note by Ninham and Colin Pask [32] more than 50 years ago how Maxwell's equations for the electromagnetic field with Planck quantization of allowed modes appear to provide a semiclassical account of nuclear interactions. The direct consequence if this idea has any relevance is that mesons would emerge as plasmons, collective excitations in an electron–positron pair-sea [31]. We then proceed to present a study that was initiated by Ninham around 1970 on excited state interaction between atoms [33]. Related self-energies and excited state interactions are, for example, essential in photobiochemistry. We finally wrap up our study with a few concluding words.

2. The Ninham, Parsegian and Weiss Semi-Classical Derivation of Lifshitz Theory

The theory due to Lifshitz was readdressed by Lifshitz, Igor Dzyaloshinskii and Lev Pitaevski [19] via some lengthy arguments that exploited Green's function techniques in quantum field theory. We outline the general ideas behind the considerably simpler semi-classical theory of dispersion interactions. The paper [21], which we follow in this Section with some changes in notation, expanded on general ideas presented by Nicolaas van Kampen and collaborators [34]. Here, we point out that Ref. [34] only considered the zero-temperature and non-retarded limit. We use the electrodynamics boundary conditions given in the book [35] that the components of $(\mathbf{E}_\omega, \mathbf{H}_\omega)$, E_x, E_y, εE_z, H_x, H_y, and μH_z (with μ the permeability) are continuous at interfaces between the media, parallel to the xy-plane at $z = 0$ and $z = d$. We are thus considering the simple enough case of two half-spaces interacting across a media. We assume that the dielectric permittivities are different, $\varepsilon_1(\omega) \neq \varepsilon_2(\omega)$ where ω denoteds the frequesncy), and the magnetic permeabilities equal to one. The solutions ($\mathbf{Y} = \sum_\omega \mathbf{Y}_\omega e^{-i\omega t}$ where $\mathbf{Y}_\omega \in \{\, \mathbf{H}_\omega, \mathbf{E}_\omega\}$) has normal mode frequencies from the wave equation [21],

$$\nabla^2 \mathbf{Y}_\omega + (\varepsilon \omega^2/c^2)\mathbf{Y}_\omega = 0, \tag{1}$$

together with $\nabla \cdot \mathbf{Y}_\omega = 0$. Here, c denotes the speed of light in the vacuum. For the separate components of $\mathbf{E}_\omega$ and $\mathbf{H}_\omega$, one assumes the form [21] $\Theta(z)e^{i(ux+vy)}$, where u and v are the wave vector components parallel to the surface, and $\Theta''(z) = \gamma^2\Theta(z)$, where the prime denotes the z-derivative. Here, $\gamma^2 = \kappa^2 - [\omega^2\varepsilon(\omega)/c^2]$ and $\kappa = \sqrt{u^2+v^2}$ is the real component of the wave vector parallel to the slab of the intermediate film. Ninham, Parsegian and Weiss showed [21] that normal modes (ω_i) are solutions of transverse magnetic (TM) and transverse electric (TE) dispersion relations,

$$D_1(\omega; d) = 1 - \Delta_{\mathrm{TM}}^2 e^{-2\gamma_2 d} = 0 = D_2(\omega; d) = 1 - \Delta_{\mathrm{TE}}^2 e^{-2\gamma_2 d}, \tag{2}$$

where

$$\Delta_{\mathrm{TE}} = \frac{\gamma_2 - \gamma_1}{\gamma_2 + \gamma_1}; \quad \Delta_{\mathrm{TM}} = \frac{\varepsilon_1\gamma_2 - \varepsilon_2\gamma_1}{\varepsilon_1\gamma_2 + \varepsilon_2\gamma_1}. \tag{3}$$

The two types of electromagnetic modes are TE and TM, and there are no TE evanescent modes. This is put into question for the Drude-plasma model for real metal surfaces, as discussed briefly in Section 3 below. The requirement of the surface-type solutions (those that are well-behaved and vanish at infinity), $\mathrm{Re}(\gamma_2) > 0$ implies that $\kappa \geq (\omega/c)\mathrm{Re}(\varepsilon_2^{1/2})$ in what follows. Ultimately, the fundamental dispersion relations in Equation (2) combine into a simple enough relation: $D = D_1 D_2 = 0$. The Gibbs interaction free energy is given by

$$F(d, T) = \frac{1}{2\pi}\int_0^\infty [F_d(r) - F_\infty(r)]r dr, \tag{4}$$

where T denotes the tempoerature; the next step is to integrate over wave vector $\mathbf{r}$,

$$F_d(r) = kT\sum_j \ln[2\sinh(\beta\hbar\omega_j(r)/2)] \tag{5}$$

(with k and $\hbar$ are the Boltzmann and the reduced Planck constants, respectively, and $\beta = 1/(kT)$) in the subsequent steps, the sum must be taken over all the available real roots of Equation (2). From this it follows that

$$\sum_j g(\omega_j) = \frac{1}{2\pi i}\oint_C g(\omega)[1/D(\omega)][dD(\omega)/d\omega]d\omega. \tag{6}$$

In the Formula (6), the path C includes the important points where D has zeros, but does not include the poles of this function (for details, see [21]). To ensure the validity of Equation (6), the functions $g(z)$ and $D(z)$ must exhibit analyticity or smoothness, where the contour C includes the relevant zeros of D, and excludes poles of $g(\omega)$. Note that $g(z)$ and $D(z)$ are assumed analytic for Equation (6) to hold. Since $g(\omega) = \ln[2\sinh(\beta\hbar\omega/2)]$ has branch cuts, it is convenient to expand it as

$$\begin{aligned} g(\omega) &= \ln[2\sinh(\beta\hbar\omega/2)] \\ &= \ln\left[e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}\right] \\ &= \frac{\beta\hbar\omega}{2} + \ln\left[1 - e^{-\beta\hbar\omega}\right] \\ &= \frac{\beta\hbar\omega}{2} - \sum_{n=1}^{\infty}\frac{1}{n}e^{-n\beta\hbar\omega} \end{aligned} \tag{7}$$

and consider each term separately. To proceed formally, we choose the path in Equation (6) starting from $-i\infty$ to $i\infty$ along the imaginary axis, then move around the right half-plane along a semicircular path with an infinity radius. Since $\varepsilon(|\omega|) \to 1$ as $|\omega| \to \infty$, $D(|\omega|) = 1$ on the semicircle and one can write

$$F_d(r) = \frac{1}{2\pi i}\int_{\infty}^{-\infty} g(i\xi)\frac{d\ln D(i\xi;d)}{d\xi}d\xi \tag{8}$$

$$= \frac{\hbar}{2}\sum_j \omega_j + \frac{\hbar}{2\pi}\sum_{n=1}^{\infty}\int_{-\infty}^{\infty}\cos(n\beta\hbar\xi)\ln D_r(i\xi;d)d\xi$$
$$-\frac{i\hbar}{2\pi}\sum_{n=1}^{\infty}\int_0^{\infty}\sin(n\beta\hbar\xi)\ln\left[\frac{D_r(i\xi;d)}{D_r(-i\xi;d)}\right]d\xi, \tag{9}$$

where D_r refers to the real roots. Using standard mathematics we exploit the identity

$$\sum_{n=1}^{\infty}\cos(nx) = \pi\sum_{n=-\infty}^{\infty}\delta(x - 2\pi n) - \frac{1}{2}, \tag{10}$$

where $\delta(\cdot)$ is the Dirac delta function. When the delta functions are substituted into the integrals, the integrations can be carried out:

$$\frac{\hbar}{2}\sum_j \omega_j + \frac{\hbar}{2\pi}\sum_{n=1}^{\infty}\int_{-\infty}^{\infty}\cos(n\beta\hbar\xi)\ln D_r(i\xi;d)d\xi = \frac{kT}{2}\sum_{n=-\infty}^{\infty}\ln D_r(i\xi_n;d), \tag{11}$$

where the Matsubara frequency $\xi_n = 2\pi kTn/\hbar$ so that

$$F_d(r) = \frac{kT}{2}\sum_{n=-\infty}^{\infty}\ln D_r(i\xi_n;d) - \frac{i\hbar}{2\pi}\sum_{n=1}^{\infty}\int_0^{\infty}\sin(n\beta\hbar\xi)\ln\left[\frac{D_r(i\xi;d)}{D_r(-i\xi;d)}\right]d\xi. \tag{12}$$

Noteworthy for dielectric functions depending on ω^2 only, one term in Equation (12) turns out to be zero by symmetry and Equation (12) reduces to

$$F_d(r) = kT\sum_{n=0}^{\infty}{}'\ln D_r(i\xi_n;d) \tag{13}$$

The prime notation here represents that the term corresponding to n = 0 is multiplied by 1/2. This equation is, for instance, valid for the so-called plasma model discussed in Section 3 just below.

3. A High-Temperature Semi-Classical Application: The Drude-Plasma Controversy

The Casimir interaction between real metal surfaces has caused controversy in the field of Casimir physics. The paper [21] discussed above could be relevant to this problem. As is known [36,37], a real metal has a finite static conductivity. The so-called Drude model is a suitable model for the optical and dielectric properties of a real metal for small frequencies. The dielectric function can be described within the Drude model as

$$\varepsilon(\omega) = 1 + \frac{4\pi i\sigma(\omega)}{\omega} = 1 - \frac{\omega_{pl}^2}{\omega(\omega + i\gamma)}. \tag{14}$$

Setting the dissipation parameter γ equal to zero is commonly called using the plasma model,

$$\varepsilon(\omega) = 1 - \frac{\omega_{pl}^2}{\omega^2}. \tag{15}$$

Notably, for metal surfaces using the Drude dielectric function, the condition used to pass from Equation (12) to Equation (13) is not fulfilled. However, the dissipation parameter has an actual physical basis. It is not zero for any real metal. Its origin is via scattering of carriers against impurities within the lattice. Importantly, when using the plasma model, one by quite a simple ad hoc decision neglects these effects and, as a result, the static conductivity becomes infinite. In Ref. [36] it is demonstrated how including the dissipation parameter has a critical effect on the predicted interaction at large surface separations, where temperature effects impact the results strongly. The plasma model predicts a result coinciding with that of the classical Gedanken experiment by Casimir between two perfectly reflecting half-spaces, while the Drude model predicts that this result is reduced by a factor of two. To understand how these drastic effects occur, one needs to look at the TM and TE normal modes involved in the problem. When dissipation is included, there are also TE evanescent modes. At separations where the temperature is essential, the contribution to the interaction from these TE evanescent modes completely cancels those from the TE propagating modes. It is known that experimental results in general agree better with the zero-temperature results between real metal surfaces and well enough with the zero-temperature result for the Casimir Gedanken experiment. The agreement is better still with the theoretical room-temperature result obtained when using the so-called plasma model. This was the seed of the long-standing controversy in the field. The finite temperature Casimir effect between metallic surfaces is a complex phenomenon, and care has to be taken about the electrostatic patch potentials, which have caused uncertainties in the actual interpretation of the data in experiments. Different theoretical groups have found fundamentally different results [36,38]. A particularly useful aspect of the original Lamoreaux experiment [39] was that it was carried out at large enough separations where finite temperature corrections can be expected. Steve Lamoreaux with collaborators later presented results using a similar experimental setup where separations were varied from 0.7 to 7 µm [40]. The theoretical predictions based upon the Drude model were found to agree with the observed results to acceptable accuracy. Let us stress, however, that other experiments [41–45] (more references can be found in the recent review by Vladimir Mostepanenko and Galina Klimchitskaya [46]), yielded results in quite good accordance with the plasma model rather than the Drude model. The reason for contradictory results (both theoretical and experimental) is not known to the authors of the present paper. There is still a need for more experiments and theoretical analysis focusing on Casimir–Lifshitz forces in different systems that include interacting conducting (metallic) objects. However, it is not the purpose of the current study to explore this problem. For one side of this long story (and relevant references), we refer to a very recent paper by Mostepanenko and Klimchitskaya [46]; see also [47]. For another side of the story, one could, for example, consult the well-explaining paper by Sernelius [37]. More information can be found in elsewhere [48–51]. But, perhaps, a correct calculation for high-temperature/large-separation Casimir force between real metal surfaces has still not been carried out. The solution might from a fundamental point of view, if perhaps not necessary from a practical point of view, involve both the use of our Equation (12) and the inclusion in the theory of any intervening plasma as in the following Section 4.

4. Another Intriguing Semi-Classical Story: Casimir Interaction Energy across a Plasma

Researchers have been looking into Casimir forces over time because of a fundamental role of those forces in electron stability, particle physics, and nuclear interactions [52–54]. We recently looked at a Casimir–Yukawa problem that is similar to the classic story of electron stability, often known as "the Casimir mousetrap" [54]. This problem explores how negative charges on an electron surface create a repulsive force between surface parts, which has to be counteracted by an attractive force to retain a finite electron radius. Casimir proposed that the attractive Poincaré stresses could be caused by the zero-point energy present in electromagnetic vacuum fluctuations [54]. Nevertheless, the study of Timothy Boyer and others showed that although the interaction's magnitude was correct, it had the wrong sign and resulted in a repulsive force [54]. Other relevant models, such as the dielectric ball, also exhibit their respective problems, some of which are still triggering discussions recently. Around 50 years ago, Ninham and Pask [32] found that the zero-temperature Casimir vacuum fluctuation energy was enough to provide the binding energy of nucleons in a nucleus. At finite temperatures, the expression (4) discussed in Section 2 reads [19]

$$F(d,T) = \frac{kT}{\pi}\sum_{n=0}^{\infty}{}' \int_0^\infty dq\, q \ln[1 - e^{-2d\sqrt{q^2+\xi_n^2/c^2}}]. \tag{16}$$

Explicitly, in vacuum (i.e., in the complete absence of an intervening electron–positron plasma), the following useful expansion [31,52,55,56] were derived,

$$F(d,T) \approx \frac{-\pi^2\,\hbar c}{720 d^3} - \frac{\zeta(3)k^3T^3}{2\pi\hbar^2c^2} + \frac{\pi^2 d k^4 T^4}{45\hbar^3c^3} + \cdots, \tag{17}$$

where zeta function $\zeta(3) \approx 1.202$. One observes that the initial term corresponds to the attractive zero temperature Casimir result. The third term in this expression corresponds to a black body radiation energy (in vacuum and at equilibrium). More than twenty years ago, Ninham and one of the authors of this paper discussed how this term opposes the attractive Casimir term [52]. The remaining term is a chemical potential term that in the Gibbs free energy is well recognized as being due to an electron–positron plasma formed from the photons inside the nuclear gap $(e^- + e^+ \leftrightarrow \gamma)$ [57]. The second term can be analysed using the known density of an electron–positron plasma [57],

$$\rho_- + \rho_+ = \frac{3\zeta(3)k^3T^3}{\pi^2\hbar^3c^3}. \tag{18}$$

For a pair of perfectly conducting plates, the Casimir interaction energy across an electron–positron plasma is

$$F(d,T) = \frac{kT}{\pi}\sum_{n=0}^{\infty}{}' \int_0^\infty dqq \ln\left[1 - e^{-2d\sqrt{q^2+(\xi_n/c)^2+\kappa^2}}\right], \tag{19}$$

Recall that $\kappa = \omega_p/c$, where ω_p denotes the plasma frequency. For any separation at high enough temperatures, or for any finite temperature at large enough separations, it follows [52,55,56] an expansion of the form,

$$F(d,T) = -\frac{kT\kappa}{4\pi}\frac{e^{-2\kappa d}}{d}\left[1 + \frac{1}{2d\kappa}\right] - \frac{(kT)^2 e^{-2\eta d}}{\hbar c}\frac{e^{-\rho^*\eta d}}{d} + \mathcal{O}(e^{-4\eta d}), \tag{20}$$

where $\rho^* = \rho\, e^2\hbar^2/(\pi m_e k^2\, T^2)$, $\eta = 2kT/(\hbar c)$ and κ is defined above. Both the $n = 0$ and $n > 0$ terms behave similarly to the Yukawa potential [31,56]. Both provide contributions to the Casimir–Yukawa binding energy, depending on the separation (about 0.9 MeV from the $n = 0$ term and about 3.6 MeV from the $n > 0$ term), and surprisingly close to the experimentally observed binding energy per nucleon (1.1 MeV to about 8.8 MeV) [31]. The idea that there ought to be some kind of link between electromagnetic and nuclear forces goes back to Richard Feynman (via private communication in the late 1960s between Ninham and Freeman Dyson, who told Ninham that Richard Feynman had believed there ought to be a connection between electromagnetic theory and nuclear interactions). This idea was first explored by Ninham and Pask in early 1970s [32]. We have revived and expanded on this idea in a series of publications [52,55,56]. The explicit derivation of meson mass, nuclear binding energy and lifetimes [58] were recently discussed at length in Ref. [31].

5. Semi-Classical Derivation of Resonance Interaction between Exited State Atom Pair

The semi-classical formalism was also able to describe in detail the ground state van der Waals potentials between a pair of molecules, or between a molecule and a surfaces [23]. Here, as one in some sense more controversial example [33,59–62], we explore what predictions come out from semi-classical theory for the resonance interaction energy between two identical atoms in an excited configuration. The results in this Section were, in the zero-temperature limit, derived about 50 years ago by Ninham, John Mitchell, and others, and finally, after deep contemplation and a final extension to finite temperatures [33], published 20 years ago. Notably, the results are, in the non-retarded limit, identical to the perturbation theory results [60–63], but in the retarded and finite-temperature limits, non-oscillatory results are found. This contrast against the oscillatory long-range retarded resonance interaction obtained from perturbation theory [60,61].

The normal mode expression used to calculate ground state van der Waals interactions in the case of two identical atoms in air,

$$1 - \alpha(1|\omega)\alpha(2|\omega)T(d|\omega)^2 = 0, \tag{21}$$

can be separated into one anti-symmetric and one symmetric part. Here, $T(d|\omega)$ is the field susceptibility [59] in a material with dielectric function $\varepsilon(\omega)$, and $\alpha(j|\omega)$ represent the polarizability of atom j. The excited symmetric state has a substantially shorter lifetime than the excited anti-symmetric state, which can cause the system to end up in an excited anti-symmetric state [33]. The first-order dispersion energy of such an anti-symmetric state comes from

$$U(d) = \hbar[\omega_r(d) - \omega_r(\infty)], \tag{22}$$

where ω_r denotes resonance frequency. The solution of Equation (21) is the pole of the anti-symmetric part (of the underlying Green's function). We change the integration path around this pole to obtain an expression for the first order excited state resonance interaction energy,

$$U(d) = (\hbar/\pi)\int_0^\infty d\xi \ln[1 + \alpha(1|i\xi)T(d|i\xi)]. \tag{23}$$

As pointed out in the past, any finite temperature systems can approximately be dealt with in the same way as for the corresponding ground state problem [55,64]. The temperature (T) dependence follows when replacing the integration over imaginary frequencies by a summation over discrete frequencies [14]. The leading term, at large separation when the modes in the ($\pm$;x) branch are excited, is

$$U(d,T) \simeq \pm\frac{2kT}{d^3}\sum_{n=0}^{\infty}{}'\alpha(i\xi_n)e^{-xn}[1 + xn + x^2n^2], \tag{24}$$

where $x = 2\pi kTd/(\hbar c)$. In a standard way we approximate the polarizability with $\alpha(0)$ at large enough separations. Within this approximation, the resonance free-energy is [33],

$$U(d,T) \simeq \pm\frac{2kT\alpha(0)}{2d^3(e^x-1)^3}[1+e^{3x}-e^x(1+2x-2x^2)+e^{2x}(-1+2x+2x^2)]. \tag{25}$$

For small values of x, this free energy of resonance interaction goes as $1/d^4$. However, for any finite temperature, the long-range interaction within the Ninham model is dominated by the $n=0$ term. This term is here

$$U(d,T)_{n=0} = \pm kT\alpha(0)/d^3. \tag{26}$$

This manifestation of the correspondence principle is identical in nature to the result obtained for the retarded van der Waals interaction between two ground-state atoms [55,64]. This highlights that the quantum nature of light has an essential role behind the softening of intermolecular interactions between ground state or excited state atoms (and indeed in the same way for Lifshitz interactions between macroscopic surfaces).

6. Discussions and Future Outlooks

This concise review primarily aims to engage an insightful discussion concerning the semi-classical theory of interactions with ground and excited state van der Waals, Lifshitz, and Casimir forces. This paper also aims to shed new light on a small, but missing, element of information that might provide some understanding to settle the Drude-plasma controversy. To be more precise, as we have already discussed in the study by Ninham, Parsegian, and Weiss [21], the conventional Lifshitz theory left out one extra term. Further investigations of the Casimir effect at high-temperatures/short-range regimes may offer more evidence for its potential influence in both meson and atom–atom physics. The modern research on van der Waals, Lifshitz, and Casimir interactions was pioneered by Ninham and Parsegian more than 50 years ago. Their respective groups demonstrated how to use the complicated Lifshitz theory and how to derive it in a much-simplified way. Researchers from around the world have developed the field for the last 50–60 years (notably, Russian researchers, including Yurii Barash and Vitaly Ginzburg [65], presented some classic works that are similar to those that came from Ninham's group in Australia). However, it is still an intensive active research field [36,46]. The field was, for instance, energized by Michael Elbaum and Michael Schick, who predicted that ice can have a nanometer sized premelted water layer on an ice surface caused by van der Waals, Lifshitz, intermolecular forces [66]. In general surface charges, ions, and impurities can induce water films many orders of magnitude thicker [67–69]. The effects caused by ionic interactions are in general complicated enough, due partly to the fact that the polarizability of ions leads to a non-linear coupling of van der Waals and ionic forces leading to the macroscopic double-layer and Lifshitz forces acting across salt solutions [70–75]. An impact from such intermolecular forces has also been proposed for frost heaving [76] and thunder cloud charging [77–79]. Ice melting at surfaces and interfaces could be relevant as habitats for life on planets and moons in permafrost regions, but also on other planets and moons in the solar system and beyond [80] (for more discussions on planetary science, see [81–83]). The reverse reaction with ice forming on a water surface via Lifshitz interactions was ruled out by the study of Elbaum and Schick [84]. However, in contrast, recent re-investigations of the optical properties of water and ice suggest such a role [85,86]. Following along these lines, we investigated how the Lifshitz interaction can contribute to some geophysical effects, including ice layer formation on gas hydrate surfaces [87]. We have recently proposed such dispersion interactions as potential energy sources behind a secondary ice growth mechanism on partially melted ice clusters within mist, fog, and potentially also in clouds [88]. The contributions from intermolecular forces to geophysics is an evolving research field with essential contributions from Luis McDowell and collaborators [86,89].

Dispersion interactions between particles and surfaces occur at finite temperatures and in the presence of a background plasma. This is not only of vital importance for various biological applications and catalysis, but it may also surprisingly enough be of interest for hidden aspects in fundamental quantum electrodynamics. All interactions between particles take place in the presence of the plasma of the fluctuating electron–positron pairs; constantly created and annihilated. This is particularly true for the interaction between nuclear particles. Strong similarities were found, suggesting a potential role for screened Casimir forces as one major contribution to the nuclear interaction. When non-relativistic plasma [56] is used, the relativistic energy, mc^2, enters the interaction energy in a quite an intriguing way: it replaces the temperature. This indicates that there could be some interesting physics hidden in this problem, and we may need to use the relativistic mass from the beginning. To make further progress, one seems may need to extend these quite simple consideration to include a relativistic plasma response function and to include magnetic (spin) susceptibilities. These are problems of the same importance as occurring in physical chemistry [90]. A fundamental ansatz commonly used, assumes that all electrostatic interactions (generally analysed in a nonlinear theory) and electrodynamic interactions (often treated within a linear approximation) can be treated separately. This, in general, is in violation of the fundamental physical laws [90]. For further progress, one needs to carefully ponder the foundations of the theory of these attractive and repulsive intermolecular interactions [91].

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