Chapter 1
Introduction

Electromagnetic fluctuations are related to one of the most fundamental phenomena in nature, namely Brownian motion. In [1–4], the nature of this motion is discussed, and its statistical features are investigated. Studies of the thermal radiation from materials have played an important role in the history of physics. It is enough to mention that quantum mechanics originated from attempts to explain paradoxical experimental results related to black body radiation. In 1900, Max Planck used quantum theory to explain the puzzling nature of the spectral density of thermal far-field radiation. However, Planck realized that the situation becomes more complex in the near-field region, when the distance from the surface of the body becomes smaller than the characteristic wavelength of thermal radiation. In the early 20th century, the spectral properties of thermal electromagnetic fluctuations were reliably studied in two limiting cases. In the first case, which corresponds to the quasistationary region of the spectrum, the Nyquist formula was obtained, which describes the spectral intensity of noise in an arbitrary passive one-port with a given impedance. In the second case, the Planck and Kirchhoff formulas were obtained, which describe the energy spectral density and the equilibrium radiation intensity. In the middle of the 20th century, Rytov created the general correlation theory of electromagnetic fluctuations on the basis of Maxwell's equations [5–7]. From Rytov's theory, one can obtain the spectrum of fluctuations in the system for arbitrary relation between its significant dimensions and characteristic wavelength of thermal radiation field. In this case, the Nyquist's and Kirchhoff's laws follow as two limiting cases. A remarkable contribution to the theory of fluctuation phenomena is the fluctuation-dissipation theorem established by Callen and Welton [8], which connects the spectral density of the fluctuations of the dynamic system that are characteristic of its dissipative properties.

The study of electromagnetic fluctuations is an important part of modern fundamental and applied science, because it is precisely the fluctuations of the electromagnetic field that determine a large class of important physical phenomena, such as the van der Waals interaction; the Casimir force, which can be considered as a special

A.I. Volokitin and B.N.J. Persson, *Electromagnetic Fluctuations at the Nanoscale*,
NanoScience and Technology, DOI 10.1007/978-3-662-53474-8_1

case of the van der Waals interaction; radiative heat transfer and Casimir friction between bodies separated by a vacuum gap; the capture of atoms, molecules and coherent material states by electromagnetic traps; and a number of major physicochemical phenomena near the surface of condensed media, such as the adsorption and desorption of atoms and molecules. Electromagnetic fluctuations lead to a change in the conditions and characteristics of the spontaneous photon emission of atoms and molecules near surfaces, the shift of their energy levels, and the complete or partial removal of degeneracy, which can substantially change the dynamics of the phenomena. We emphasize that a study of resonance states in the spectra of thermally stimulated fields allows the eigenmodes of the system to be discovered, i.e., its volume and surface polaritons, whose properties are totally determined by the electrodynamic and geometric characteristics of the system. At present, in connection with new experiments, interest in Casimir physics is being revived. Figure 1.1 illustrates the connection between the Casimir physics and Brownian motion.

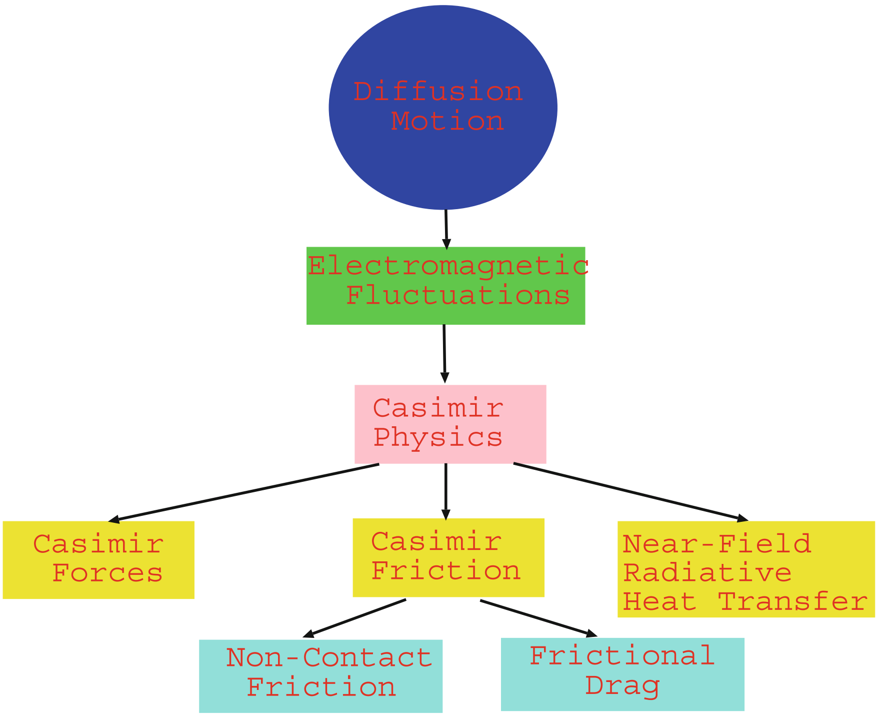

Fig. 1.1 Relationship between Casimir physics and Brownian motion. The electromagnetic fluctuations are the cornerstone of the Casimir physics, which includes Casimir forces, Casimir friction and near-field radiative heat transfer. These fluctuations are described in the fluctuational electrodynamics by introducing a 'random' field into the Maxwell equation (just as, for example, one introduces a 'random' force in the theory of Brownian motion)

In the past, the non-radiative near-field part of the electromagnetic radiation was usually ignored, because it plays no role in the far-field properties of emission from planar sources. Nevertheless, recent interest in microscale and nanoscale radiative heat transfer [9–15], together with the development of local-probe thermal microscopy [17, 18] has raised new challenges. These topics, and the recent progress in detecting the non-contact friction force on a subattonewton level [19–21, 23–27], and the observation of coherent thermal emission from materials [28–38], have the substantial role of the non-radiative (evanescent) thermal electromagnetic field in common. The physical mechanisms and phenomena occurring at the nanoscale have received significant attention over the last decade because of improvements in nanostructure fabrication, the development of advanced scanning probe microscopy and interest in basic research. The findings have implications for topics such as thermophotovoltaics, nano-electromechanical systems, heat-assisted magnetic recording, heat-assisted litography, the design of devices that rely on resonant or coherent heat emission, and nano-antennas.

1.1 Fluctuations and the Physical Origin of the van der Waals and Casimir Forces

There are four known fundamental forces: electromagnetism, gravity, and weak and strong interactions. Weak and strong interactions manifest themselves on length scales in the order of the size of a nucleus; whereas, at larger distances, electromagnetism and gravity prevail. It may therefore come as a surprise that two macroscopic non-magnetic bodies with no net electric charge (or charge moments) can experience an attractive force much stronger than gravity. This force was predicted in 1948 by Hendrik Casimir [39], and now bears his name. The existence of this force is one of the few direct macroscopic manifestations of quantum mechanics; others are superfluidity, superconductivity, kaon oscillations, and the black body radiation spectrum.

The origin of both the van der Waals and Casimir forces is connected to the existence of quantum and thermal fluctuations. Two neutral particles have fluctuating dipole moments resulting from quantum or thermal effects, which, for the particle separation d, lead to a d^{-6} interaction energy. This long-range attraction is often the dominant interactions between atoms and molecules. Physically, this attraction arises as shown in Fig. 1.2a: whenever one particle acquires a spontaneous dipole moment $\mathbf{p}_1$, the resulting dipole electric field (black lines) polarizes the adjacent particle to produce an induced dipole moment $\mathbf{p}_2 \sim d^{-3}$. Assuming positive polarizabilities, these two dipoles are oriented so as to attract each other, with an interaction energy that scales as d^{-6}. This leads to the van der Waals ‘dispersion’ force, and similar considerations apply to particles with permanent dipole moments that can rotate freely. The key to a more general theory of the Casimir interaction is to understand that this d^{-6} scaling of van der Waals forces is based two crucial approximations,

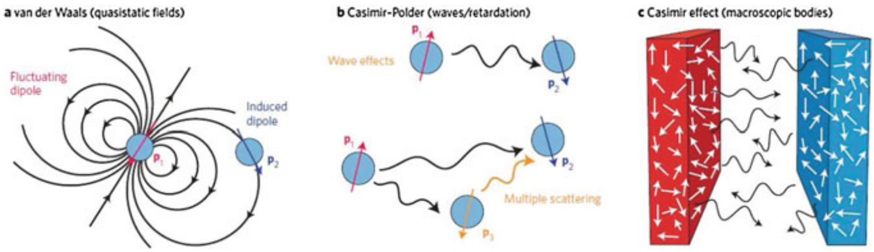

Fig. 1.2 Relationship between van der Waals, Casimir-Polder and Casimir forces, whose origins lie in the quantum fluctuations of dipoles. **a**, A fluctuating dipole $\mathbf{p}_1$ induces a fluctuating electromagnetic dipole field, which in turn induces a fluctuating dipole $\mathbf{p}_2$ on a nearby particle, leading to van der Waals forces between the particles. **b**, When the particle spacing is large, retardation/wave effects modify the interaction, leading to Casimir-Polder forces. When more than two particles interact, the non-additive field interactions lead to a breakdown of the pairwise force laws. **c**, In situations consisting of macroscopic bodies, the interaction between the many fluctuating dipoles present within the bodies leads to Casimir forces. From [64]

that are not always valid: it neglects wave effects (quasi-static approximation), and also neglects multiple scattering if there are more than two particles. The quasi-static approximation assumes that the dipole moment $\mathbf{p}_1$ polarizes the second particle instantaneously, which is valid if d is much smaller than the typical wavelength of the fluctuating fields. For such separations, retardation effects are negligible. In this separation region, the dispersion force is usually called the van der Waals force. This is a non-relativistic quantum phenomenon and its theory was pioneered by London (1930) [40]. However, the finite speed of light must be taken into account when d is much larger than the typical wavelength, as shown in Fig. 1.2b, and it turns out that the resulting Casimir-Polder interaction energy asymptotically scales as d^{-7} for large values of d. At such separations, the dispersion forces are usually called *Casimir* forces (for interaction between two macroscopic bodies) or *Casimir-Polder* forces (for atom-atom and atom-wall interactions). These are both relativistic and quantum-mechanical phenomena first described by Casimir (1948) [39] and by Casimir and Polder (1948) [41], respectively. More generally, the interaction is not a simple power law between these limits, but instead depends on an integral of fluctuations at all frequencies scaled by a frequency-dependent polarizability of the particles.

The presence of more than two particles further complicates the situation because multiple scattering must be considered (Fig. 1.2b). For example, with three particles, the initial dipole $\mathbf{p}_1$ will induce polarizations $\mathbf{p}_2$ and $\mathbf{p}_3$ in the other two particles, but $\mathbf{p}_2$ will create its own field that further modifies $\mathbf{p}_3$, and so on. Thus, the interaction between multiple particles is generally non-additive, and there is no two-body force law that can simply be summed to incorporate all interactions. Multiple scattering is negligible for a sufficiently dilute gas or for weak polarizabilities, but it becomes very important for interactions between two (or more) solid bodies, which consist of many fluctuating dipoles that all interact in a complicated way through the electromagnetic radiation (Fig. 1.2c). When these multiple scattering effects are combined with wave retardation in a complete picture, they yield the Casimir force.

Hendrik Casimir based his prediction on a simplified model involving two parallel perfectly conducting plates separated by a vacuum. Although the Casimir force arises from electromagnetic fluctuations, real photons are not involved. Quantum mechanically, these fluctuations can be described in terms of virtual photons of energy that are equal to the zero-point energies of the electromagnetic modes of the system. By considering the contribution of the electromagnetic field modes to the zero-point energy (U) of the parallel plate configuration, Casimir predicted an attractive force between the plates. Because only electromagnetic modes that have nodes on both walls can exist within the cavity, the mode frequencies (ω) depend on the separation between the plates, giving rise to a pressure of $P_0 = -\partial U_0/\partial d$:

$$U_0(d) = -\frac{\pi^2 \hbar c}{720 d^3}, \quad P_0(d) = -\frac{\pi^2 \hbar c}{240 d^4} \tag{1.1}$$

where c is the vacuum speed of light and $\hbar$ is the reduced Planck's constant. The force in this case is attractive because the mode density in free space is larger than that between the plates. Ideal metals are characterized by perfect reflectivity at all frequencies, which means that the absorption wavelength is zero. Thus, the results (1.1) are universal and valid at any separation distance. They do not transform to the non-relativistic London forces at short separations. Due to the difference in these early theoretical approaches to the description of the dispersion forces, the van der Waals and Casimir-Polder (Casimir) forces were originally thought of as two different kinds of forces rather than two limiting cases of a single physical phenomenon, which is how they are presently understood.

A unified theory of both the van der Waals and Casimir forces between plane parallel material plates in thermal equilibrium separated by a vacuum gap was developed by Lifshitz (1955) [42]. Lifshitz's theory describes dispersion forces between dissipative media as a physical phenomenon caused by the fluctuating electromagnetic field that is always present in both the interior and the exterior of any medium. To calculate the fluctuating electromagnetic field, Lifshitz used Rytov's theory [5–7]. Rytov's theory is based on the introduction into the Maxwell equation of a 'random' field (just as, for example, one introduces a 'random' force in the theory of Brownian motion). The fundamental characteristic of the random field is the correlation function, determining the average value of the product of component of this field at two different points in space. Initially, Rytov found this correlation function using a phenomenological approach. Later, Rytov's formula for the correlation function of the random field was rigorously proved on the base of the fluctuation-dissipation theorem. According to the fluctuation-dissipation theorem, there is a connection between the spectrum of fluctuations of the physical quantity in an equilibrium dissipative medium and the generalized susceptibilities of this medium, which describe its reaction to an external influence. Using the theory of the fluctuating electromagnetic field, Lifshitz derived general formulas for the free energy and force of the dispersion interaction. In the limit of dilute bodies, these formulas describe the dispersion forces acting between atoms and molecules. In the framework of the Lifshitz theory, material properties are represented by the frequency dependent dielectric permittivities and atomic properties by the dynamic atomic polarizabilities. In the limiting cases of small and large separation distances, in comparison with the characteristic absorption wavelength, the Lifshitz theory reproduces the results obtained by London and by Casimir and Polder, respectively. It also describes the transition region between the non-relativistic and relativistic limits.

Both quantum and thermal fluctuations contribute to the Casimir force. The general theory of Casimir-van der Waals forces was developed in [43] using quantum field theory. This theory confirmed the results of Lifshitz's theory. Quantum fluctuations dominate at small separation ($d < \lambda_T = c\hbar/k_B T$) and thermal fluctuations dominate at large separation ($d > \lambda_T$). Casimir forces due to quantum fluctuations have long been studied experimentally [44–56]. However, Casimir forces due to thermal fluctuations were measured only recently, and these measurements confirmed Lifshitz's theory [57]. At present, interest in Casimir forces is increasing since it was shown that it is possible to measure these forces with high accuracy [44–57]. Casimir forces often dominate the interaction between nanostructures, and can result in adhesion and mechanical failure between moving parts in small devices such as micro- and nano-electromechanical systems [55, 56, 58, 59] (MEMS and NEMS). Due to this practical interest and the fast progress in force detection techniques, experimental [57, 60–63] and theoretical [64, 65] investigations of Casimir forces have experienced an extraordinary 'renaissance' in the past few years. Various corrections to these forces have been studied, such as finite conductivity [66], or temperature corrections [67, 68].

The Lifshitz theory was formulated for systems at thermal equilibrium. At present, there is an interest in the study of systems outside of the thermal equilibrium, in particular, in connection with the possibility of tuning the strength and sign of the interaction [69–71]. Such systems also present a way to explore the role of thermal fluctuations, which are usually masked at thermal equilibrium by the $T = 0$ K component, which dominates the interaction up to very large distances, where the interaction force is very small. In [71], the Casimir-Polder force was measured at very large distances, and it was shown that the thermal effects on the Casimir-Polder interaction agree with the theoretical prediction. This measurement was taken outside of thermal equilibrium, where thermal effects are stronger.

The fluctuating electromagnetic field in the Lifshitz theory is the classical analog of vacuum (zero-point) oscillations in the field-theoretical approach developed by Casimir. van Kampen et al. (1968) [72], Ninham et al. [73], Gerlach (1971) [74] and Schram (1973) [75] narrowed the distinction between the Casimir and Lifshitz approaches. They obtained the Lifshitz formulas for free energy and force between two non-dissipative material plates as the difference between the free energies of zero-point and thermal oscillations in the presence and in the absence of plates. The eigenfrequencies of these oscillations were found from the standard continuity boundary conditions for the electric and magnetic induction fields on the surfaces of the dielectric plates. Later, Barash and Ginzburg (1975) [76] generalized this approach for the case of plates made of dissipative materials in thermal equilibrium with a heat reservoir. This generalization was presented by Millonni (1994) [45] and by Mostepanenko and Trunov (1997) [77]. The applicability of the Lifshitz formula to dissipative materials was also demonstrated using the scattering approach (Genet Lambrecht and Reynaud 2003) [78].

The theoretical foundations of the Casimir interaction are based on two approaches. The first approach is based on the theory of the equilibrium electromagnetic fluctuations in the media. In the second approach, the Casimir effect is a vacuum quantum effect resulting from the influence of external conditions and is described by quantum field theory. In this case, boundary conditions are imposed (in place of material boundaries) that restrict the quantization volume and affect the spectrum of zero-point and thermal oscillations. In fact, the two different approaches can be reconciled. There are derivations of the Lifshitz formulas and more general results in different media where the dispersion force is viewed as a vacuum quantum effect [79, 80]. The common roots in the theory of electromagnetic oscillations relate the Casimir effect to other fluctuation phenomena, such as the radiative heat transfer through a vacuum gap and the Casimir friction [11]. However, its origin in quantum field theory relates the Casimir effect to other quantum vacuum effects such as the Lamb shift and the anomalous magnetic moment of an electron, where virtual particles play an important role [81].

During the last few years, far-reaching generalizations of the Lifshitz formulas were obtained that express Casimir energy and the force between two separated bodies of arbitrary shape in terms of matrices of infinite dimensions. This is often referred to as the representation of Casimir energy in terms of functional determinants [82–84] or in terms of scattering matrices [85, 86]. Overviews of the Casimir effect are given, for example, in [60, 87–90].

1.2 Radiative Heat Transfer

The radiative heat flux per unit area between two black bodies separated by $d \gg \lambda_T = c\hbar/k_B T$ is given by the Stefan-Boltzmann law

$$S = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}\left(T_1^4 - T_2^4\right), \tag{1.2}$$

where T_1 and T_2 are the temperatures of solid 1 and 2, respectively, and c is the velocity of light. In this limiting case, the heat transfer between two bodies is determined by the propagating electromagnetic waves (far field) radiated by the bodies and does not depend on the separation d (see Fig. 1.3). These propagating waves always exist outside any body due to thermal and quantum fluctuations of the current density inside the body. Quantum fluctuations are related to the uncertainty principle, and exist also at zero temperature. Thermal fluctuations are due to the irregular thermal motion of the particles in the medium, and vanish at zero temperature. The electromagnetic field created by this fluctuating current density exists not only in the form of propagating waves but also in the form of evanescent waves, which are damped exponentially with the distance away from the surface of the body. This fluctuating electromagnetic field exists even at zero temperature, generated by quantum fluctuations. For an isolated

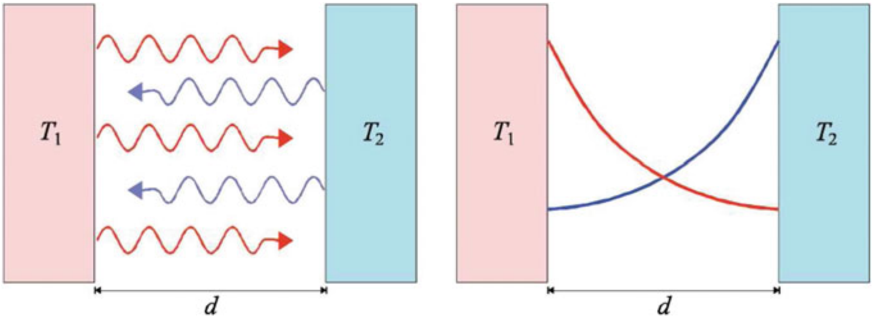

Fig. 1.3 There are two modes for exchange of heat between two surfaces separated by vacuum: **a** conventional radiative heat transfer via propagating electromagnetic waves; and **b** photon tunneling via evanescent waves

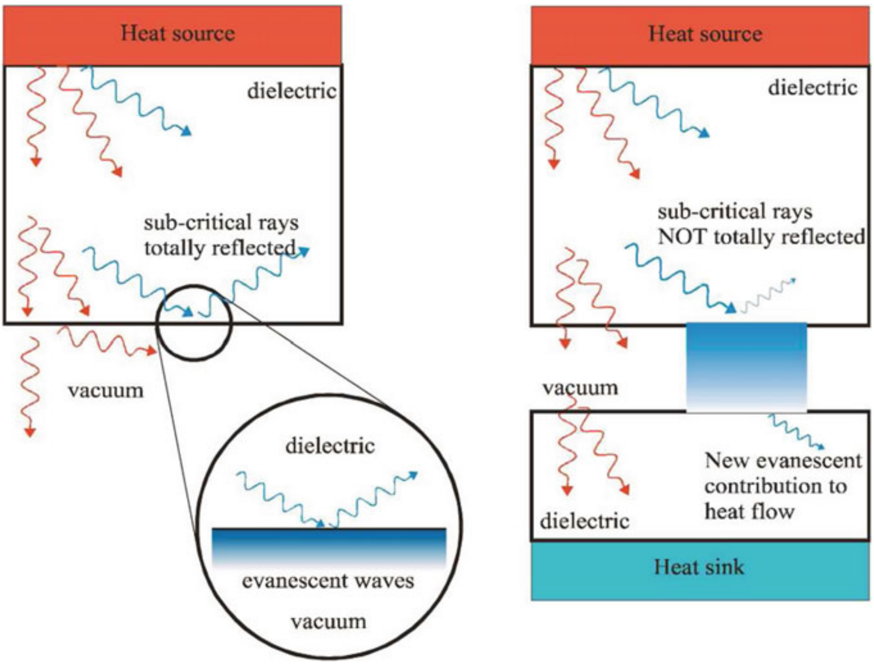

Fig. 1.4 Evanescent waves play no role in thermal radiation from a hot dielectric surface to vacuum (*left*), but evanescent waves can carry heat from a hot to a cold dielectric surface (*right*)

body the evanescent waves do not give any contribution to the energy radiation, which is determined by Stefan-Boltzmann law. However, for two solids separated by $d < \lambda_T$, the heat transfer may increase by many orders of magnitude due to the evanescent electromagnetic waves; this is often refereed to as photon tunneling. The concept of photon tunneling can be neatly illustrated by considering a transparent dielectric such as glass (see Fig. 1.4). Within the dielectric, black body radiation has

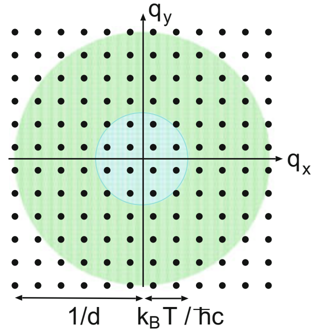

Fig. 1.5 At short distances, evanescent states dominate in phase space: propagating photon modes carry heat flux within the inner circle (with the radius $k_B T/\hbar c$), evanescent modes within the outer circle (with the radius d^{-1})

a higher density than in the vacuum, as can be seen from (1.2); if the velocity of light is reduced, the density of radiation increases. The extra radiation is contained in waves that have large wave vectors, q parallel to the surface. The normal component of the wave vector, which in the vacuum region is given by $p_z = \sqrt{(\omega/c)^2 - q^2}$, will be pure imaginary for $q > \omega/c$, where ω is the electromagnetic wave frequency. This means that the photons with $q > \omega/c$ can not escape from the body, and will be totally reflected from the surface. This phenomenon is known as total internal reflection. Thus, the surface reflects just the right amount of radiation to ensure that the intensity of the black body radiation emerging into vacuum does not exceed that allowed by (1.2).

It is well known that a second dielectric, if close enough to the first one, will modify the internal reflection condition so that some of the 'evanescent photons' tunnel across into the second medium.

Let us consider the electromagnetic field at a distance d from a surface. The region in the q-space occupied by the propagating waves is $q < k_B T/\hbar c$. The phase space region occupied by the evanescent waves is $q < d^{-1}$. Thus, as illustrated in Fig. 1.5, at short distance $d \ll \lambda_T$ the number of photon states available to conduct heat may be much larger for the evanescent waves than for the propagating waves. At low temperatures (a few Kelvin), it is possible for photon tunneling to dominate the heat transfer even at a spacing of a few mm, see Table 1.1.

A great deal of attention has been devoted to the radiative heat transfer due to evanescent waves in connection with scanning tunneling microscopy (STM), and scanning thermal microscopy (SThM), under ultrahigh vacuum conditions [9–15, 17, 18]. It is now possible to measure extremely small amounts of heat transfer into small volumes [91]. STM can be used for local heating of the surface, resulting in local desorption or decomposition of molecular species, and this offers further possibilities for the control of the local chemistry at surfaces by STM [92].

The problem of the radiative heat transfer between two flat surfaces was considered many years ago by Polder and Van Hove [93]; Levin and Rytov [94]; and, more recently, by Loomis and Maris [95]; Pendry [12]; Volokitin and Persson [13–15]; and Joulain et al. [9]. Polder and Van Hove were the first to obtain the correct formula for the heat transfer between two flat surfaces. In their investigation, they used Rytov's

Table 1.1 The critical distance λ_T as a function of temperature. For surface separation $d < \lambda_T$ the heat transfer is dominated by the contribution from the evanescent electromagnetic modes. At distances of a few nanometers, radiative heat flow is almost entirely due to the evanescent modes

T(K)	λ_T (μm)
1	2298.8
4.2	545.2
100	22.9
273	8.4
1000	2.3

theory [5–7] of the fluctuating electromagnetic field. Later, this formula was rederived in [95]. However, Polder and Van Hove presented their result within the local optic approximation, where the spatial variation of the dielectric function is neglected. Thus, material for which non-local optical properties (such as the anomalous skin effect) are important, and are excluded from their treatment. In general, non-local optic effects become very important for short separation between bodies when

$$d < v_F\hbar/k_BT,\ l,$$

where v_F is the Fermi velocity, and l is the electron mean free path [191, 197]. In typical cases, non-local optic effects become very important for $d < 1000$ Å [13]. In the subsequent treatment, they made numerical calculations not of the heat flux itself, but of its derivative with respect to temperature, i.e., their numerical result is valid only for small temperature differences. Pendry considered only the non-retarded limit. The first theory that included non-local optic and retardation effects was developed by Volokitin and Persson [13], who used the general theory described above. Levin and Rytov [94] used the generalized Kirchhoff's law [6] to obtain an expression for the radiative heat transfer between two good conductor surfaces. They studied the case of good conductors in detail, in both the normal and the anomalous skin effect region. Pendry [12] gave a more compact derivation of the formula for the heat flux between two semi-infinite bodies due to evanescent waves and calculated the heat transfer between a point-dipole and a surface. Volokitin and Persson [13] considered the problem of heat transfer between two flat surfaces as a particular application of a general theory of the fluctuating electromagnetic field for heat transfer between bodies with arbitrary shape. They numerically investigated the dependence of the heat flux on the dielectric properties of the bodies, both in the local optic approximation and using the non-local optic dielectric approach, and found that, for good conductors, even for very small distances, the heat flux is dominated by retardation effects. The efficiency of the radiative heat transfer depends strongly on the dielectric properties of the media. It was found in these works that the heat flux diverges as the distance decreases if the temperature difference is assumed to be kept at a constant value. These results were obtained using a macroscopic theory where the spatial variation of the dielectric function was neglected. This macroscopic theory is only valid if the separation between bodies is much larger than the interatomic distances inside the bodies. However, it is possible to determine an upper limit for the heat flux, which at short separations depends only on the properties of the materials [12] (see also Chap. 6). This result is linked to quantum information theory, which dictates that the maximal heat tunneling current in one channel is determined by the temperature alone [12, 96]. The role of non-local dielectric response for the thermal electromagnetic field near a planar surface was discussed in [13, 97].

In [12, 13, 15], it was shown that the heat flux can be greatly enhanced if the conductivities of the materials are chosen to maximize the heat flow due to photon tunneling. At room temperature, the heat flow is maximal at conductivities corresponding to semi-metals. In fact, only a thin film ($\sim$10 Å) of a high-resistivity material is needed to maximize the heat flux. Another enhancement mechanism of the radiative heat transfer can be connected with resonant photon tunneling between states localized on the different surfaces. Recently it was discovered that resonant photon tunneling between surface plasmon modes gives rise to an extraordinary enhancement of the optical transmission through sub-wavelength hole arrays [98]. The same coupling will enhance the radiative heat transfer (and the Casimir friction [99, 100]) if the frequency of these modes is sufficiently low enough to be excited by thermal radiation. At room temperature, only the modes with frequencies below $\sim 10^{14}$ s^{-1} can be excited. For normal metals, surface plasmons have much too high frequencies; at thermal frequencies, the dielectric function of normal metals becomes nearly purely imaginary, which excludes surface plasmon enhancement of the heat transfer for good conductors. However, surface plasmons for semiconductors are characterized by much smaller frequencies and by damping constants, and they can contribute significantly to the heat transfer.

Enhancement of the heat transfer due to resonant photon tunneling between surface plasmon modes localized on the surfaces of semiconductors was predicted by Mulet et al. [16] and Volokitin and Persson [14, 15]. In these cases, multiple scattering of electromagnetic waves by the surfaces of the bodies becomes important. In particular, at sufficiently small separation d, the photons go back and forth several times in the vacuum gap, building up a coherent constructive interference in the forward direction, as would occur in resonant electron tunneling. In this case, the surface plasmons on the isolated surfaces combine to form a 'surface plasmon molecule', in much the same way as electronic states of isolated atoms combine to form molecular levels. This will result in a very weak distance dependence of the heat flux, because the photon transmission probability does not depend on d in this case (see below). For large d, sequential tunneling is more likely, where a surface plasmon mode decays by emitting a photon, which tunnels to the other surface where it excites a plasmon, and then couples to the other excitations in the media and exits. Other surface modes that can be excited by thermal radiation are adsorbate vibrational modes. Especially for parallel vibrations, these modes may have very low frequencies. Adsorbate vibrational mode enhancement of the radiative heat transfer was predicted by Volokitin and Persson [14, 15] using a macroscopic approach [14] for separation $d > b$, and a microscopic approach [15] for $d < b$, where b is the interatomic distance between the adsorbates. In the latter case, the heat transfer occurs through the energy exchange between separate adsorbates. Persson et al. [92] showed that localized photon tunneling between adsorbates can be used for vibrational heating of molecules adsorbed on insulating surfaces. The heat transfer between two small particles (when the size of the particles is much smaller than separation between them) was first studied by Volokitin and Persson [13], and later by Domingues et al. [101]. It has been shown that at small separation ($d \ll \lambda_T$) the dipole-dipole interaction yields a large contribution to the heat transfer, whereas the contribution of the photon emission and absorption process is negligible. This near-field transfer between nanoparticles is analogous to the energy transfer between molecules due to the dipole-dipole coupling, known as Forster transfer [102].

The first measurements of the radiative heat transfer between two chromium bodies with flat surfaces was performed by Hargreaves [103]. However, placing two flat parallel plates at a constant separation of a few hundred nanometers was difficult to achieve. Later studies employing an indium needle in close proximity to a planar thermocouple remained inconclusive [104]. More recently, an unambiguous demonstration of near-field radiative heat transfer under ultrahigh vacuum conditions was given in [18, 105]. In the experiment, the heat transfer was measured between a gold-coated scanning tunneling microscope and a plate of gold or GaN. It was found that for tip-sample distances below 10 nm, the heat flux differs markedly from the divergent behavior predicted by macroscopic theory in which the local optic approximation is used. While the shortcomings of the local optic approximation in macroscopic theory are well known [7, 107], their manifestation in an actual experiment indicates a still unexplored potential of thermal microscopy as a new, quantitative tool for the nanometer-scale investigation of solids. Unfortunately, the geometry of the experiment in [18, 106] was too complex to allow for a quantitative comparison with theory. Even today, a constant separation of a few tens-of-nanometers between plates has not been accomplished. This problem forced most experimental groups investigating heat transfer and forces between two surfaces to switch to a plane-sphere geometry, which is much easier to align. The first measurements between two dielectric materials in the plane-sphere geometry were reported in [108, 109]. In the experiment, the heat transfer between a sphere and a plate, both made from of silica, was measured from 30 nm to 10 μm separation. It was demonstrated that surface phonon polaritons dramatically enhance energy transfer between two surfaces at small gaps. In [110], the prediction given by the theory of fluctuating electromagnetic fields was confirmed, at least for separation ranging from 30 nm to 2.5 μm. Radiative heat transfer in the extreme near field down to separation as small as two nanometers was measured in [111]. The authors observed extremely large enhancements of the radiative heat transfer in the extreme near field limit between both dielectric and metal surface. The experimental results are in excellent agreement with theoretical predictions within the framework of the fluctuational electrodynamics. Thus, the experimental data provide unambiguous evidence for the validity of the fluctuational electrodynamics and local optic approximation down to very short separation in the order of one nanometer.

1.3 Non-contact Friction

For more than 30 years physicists have been interested in how Casimir forces and radiative heat transfer are modified for bodies moving relative to each other. A number of researchers have shown that the relative motion of bodies leads to a friction force [11, 115, 117–121]. Theory predicts that the Casimir friction acts even at zero temperature, where it is determined by quantum fluctuations. However, in recent years, the existence of quantum friction was hotly debated [122–127]. A general theory of Casimir forces, Casimir friction and the radiation heat transfer between moving bodies was developed by us in [128]. This theory confirmed the correctness of the previous results obtained using quantum mechanical perturbation theory [115, 117], dynamical generalization of the Lifshitz-Rytov's theory [100, 121] and quantum field theory [129].

The problem of Casimir friction is closely related to non-contact friction between nanostructures, including, for example, the frictional drag force between electrons in 2D quantum wells [112–114], and the friction force between an atomic force microscope tip and a substrate [19–23]. A great deal of attention has been devoted to the problem of non-contact friction because of its importance for ultrasensitive force detection experiments. This is because the ability to detect small forces is inextricably linked to friction via the fluctuation-dissipation theorem. According to this theorem, the random force that makes a small particle jitter would also cause friction if the particle were dragged through the medium. For example, the detection of single spins by magnetic resonance force microscopy [130], which has been proposed 3D atomic imaging [131] and quantum computation [132], will require force fluctuations (and consequently the friction) to be reduced to unprecedented levels. In addition, the search for gravitation effects at the short length scale [133], and future measurements of the Casimir and van der Waals forces [89], may eventually be limited by non-contact friction effects.

In non-contact friction, bodies are separated by a potential barrier that is thick enough to prevent electrons or other particles with a finite rest mass from tunneling across it, but allows interaction via the long-range electromagnetic field, which is always present in the gap between bodies. Non-contact friction can be investigated using an atomic force microscope, a probe which is an extremely sharp tip attached to the elastic arm (cantilever). When scanning a surface, the tip of the cantilever slides above it at short distance. This device makes it possible to register the strength of the normal and lateral force components of the interaction between the surface and the probe-tip. Various mechanisms of non-contact friction are schematically illustrated in Fig. 1.6. If the bodies are in relative motion, the fluctuating current density inside bodies will give rise to a friction which will be denoted as the *Casimir friction*. The origin of the Casimir friction is closely connected to the van der Waals-Casimir interaction. The van der Waals interaction arises when an atom or molecule spontaneously develops an electric dipole moment due to quantum fluctuations. The short-lived atomic polarity can induce a dipole moment in a neighboring atom or molecule some distance away. The same is true for extended media, where

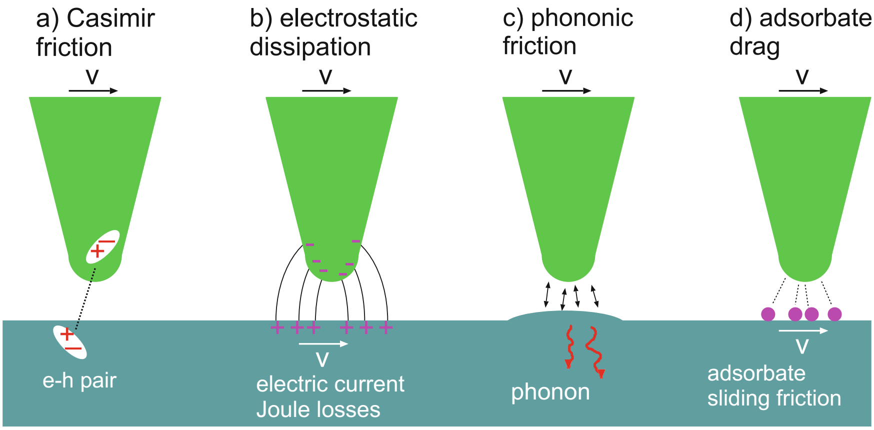

Fig. 1.6 Four different mechanisms of non-contact friction at motion of the cantilever tip parallel to the surface of a body. **a** Conservative van der Waals forces are due to the photon exchange (virtual and real) between the bodies. This process is determined by the quantum and thermal fluctuations of charge and current densities inside the bodies. In the case of a moving tip Doppler frequency shift of the emitted photons and/or time delay of the interaction leads to the Casimir friction. **b** Charged tip induces a surface image charge of opposite sign, which follows the motion of the tip and experiences the ohmic losses. That is the source of the electrostatic friction. **c** Conservative forces cause deformation of the surface. Moving deformation leads to the dissipation of energy due to emission of phonons. **d** A moving tip will induce a drag force acting on the adsorbates on surface of substrate due to the Casimir or electrostatic interaction between the tip and adsorbates. Sliding adsorbates lead to energy dissipation due to friction between adsorbates and the substrate

thermal and quantum fluctuation of the current density in one body induces a current density in the other body; the interaction between these current densities is the origin of the Casimir interaction [42, 43] (see also Chap. 5). When two bodies are in relative motion, the induced current will lag slightly behind the fluctuating current inducing it, and this is the origin of the Casimir friction (Fig. 1.6a). The van der Waals - Casimir interaction is mostly determined by exchange of virtual photons between the bodies (connected with quantum fluctuations), and does not vanish even at zero temperature. The contribution from real photons (connected with thermal fluctuations) becomes important only at large separations between bodies. On the other hand, the Casimir friction is determined by thermal or quantum fluctuations at small or large velocities, respectively. The Casimir friction at zero temperature is denoted as *quantum friction*. The Casimir friction is closely related to the Doppler effect (see Fig. 1.7). If one body emits radiation, then in the rest reference frame of the second body these waves are Doppler shifted which will result in different reflection amplitudes. Thus, photons propagating in the opposite direction will reflect differently if the reflection amplitude of the second body depends on the frequency. The same is true for radiation emitted by the second body. The exchange of 'Doppler shifted photons' is the origin of Casimir friction.

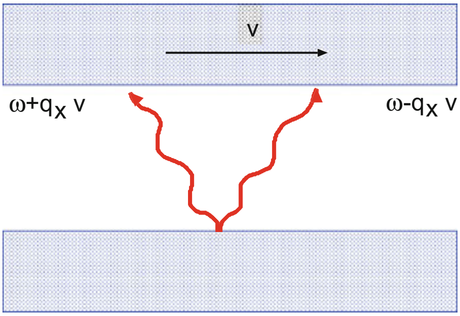

Fig. 1.7 The electromagnetic waves emitted in the opposite direction by the body at the bottom will experience opposite Doppler shift in the reference frame in which the body at the *top* is at rest. Due to the frequency dispersion of the reflection amplitude, these electromagnetic waves will reflect differently from the surface of the body at the *top*, which gives rise to momentum transfer between the bodies. This momentum transfer is the origin of Casimir friction

The presence of an inhomogeneous tip-sample electric fields is difficult to avoid, even under the best experimental conditions [21]. For example, even if both the tip and the sample were metallic single crystals, the tip would still have corners, and more than one crystallographic plane exposed. The presence of atomic steps, adsorbates, and other defects will also contribute to the spatial variation of the surface potential. This is referred to as "patch effect". The surface potential can also be easily changed by applying a voltage between the tip and the sample. An inhomogeneous electric field can also be created by charged defects embedded in a dielectric sample. The relative motion of the charged bodies will produce friction, which will be denoted as the *electrostatic friction* (Fig. 1.6b).

A moving tip will induce the dynamical deformation of surface of substrate due to the Casimir or electrostatic interaction between the tip and surface. This dynamical deformation will excite phonons in the substrate which are responsible for *phononic* mechanism of non-contact friction (Fig. 1.6c).

A moving tip will induce a drag force acting on the adsorbates on the substrate surface due to the Casimir or electrostatic interaction between the tip and adsorbates. This drag force results in a drift motion of the adsorbates relative to the substrate, and dissipation due to friction between adsorbates and substrate. This mechanism of dissipation is responsible for the adsorbate drag friction (Fig. 1.6d).

From the point of view of the quantum mechanics, the Casimir friction originates from two types of processes: (a) Excitations are created in each body with opposite momentum and the frequencies of these excitations are connected by $vq_x = \omega_1 + \omega_2$, where q_x is the momentum transfer; and (b) An excitation is annihilated in one body and created in another. The first process (a) is possible even at zero temperature, and it gives rise to a friction force, which depends cubically on sliding velocity [11, 115, 121]. The second process (b) is possible only at finite temperatures, and gives rise to a friction that depends linearly on the sliding velocity. Thus, process (b) will give the main contribution to the friction at sufficiently high temperatures, and at not too large velocities.

In contrast to the Casimir interaction, for which theory is well established, the field of Casimir friction is still controversial. As an example, different authors have studied the Casimir friction between two flat surfaces in parallel relative motion using different methods, and obtained results that are in sharp contradiction to each other. The first calculation of Casimir friction was carried out by Teodorovich [135]. Teodorovich assumed that the friction force could be calculated as the ordinary van der Waals force between bodies at rest, whose dielectric functions depend on the velocity. Such an approach is completely unjustified because it does not take into account occurrence of excitations, which are the origin of the Casimir friction. Later the same approach was used by Mahanty [136] to calculate the friction between molecules. Both theories predict wrong non-zero friction (to linear order in the sliding velocity) at absolute zero of temperature. The same nonzero linear friction at zero temperature was predicted in [137, 138]. In these works the friction force between small particle and plane surface was calculated, assuming that the friction force power is equal to the radiation power absorbed by the moving particle. From the energy conservation law it follows that in the laboratory reference frame the radiation power absorbed by moving particles is equal (with opposite sign) to the heating power inside the semi-infinite body, but it does not take into account the heating power generated inside the particle. The latter heat generation is equal to the radiation power absorbed by the particle in the rest reference frame of the particle. The right expression for the energy dissipation due to friction can be obtained as the difference between the radiation power absorbed by the particle in the rest reference frame of particle, and in laboratory reference frame [139] (see also Appendix H). A correct treatment within this approach gives a vanishing linear friction at $T = 0$ K. Schaich and Harris developed a theory [140] based on Kubo formula for the friction coefficient. This theory predicts vanishing linear friction at $T = 0$ K. However, in their calculations they made the series of unphysical approximations, and, as a result, they did not obtain the correct formula, establishing the connection of the friction coefficient with the reflection amplitude.

In [141–143], different approaches were used to calculate the friction force, and different results were obtained. The authors of these papers did not present sufficient details in order to determine exactly where there is an error. In the work by Polevoi [142], the friction force was determined from the calculation of the energy dissipation due to friction. However, as above, such an approach requires delicate considerations. All these papers predict a vanishing friction in the non-retarded limit, which formally can be obtained in the limit of infinite light velocity $c \to \infty$. However, at least for short distances, one can neglect the retardation effects when calculating Casimir friction, as well as Casimir forces. Probably, the errors of these works are related to the fact that the authors took into account the relativistic effects, but they neglected the non-relativistic effects. Pendry [115] assumed zero temperature and neglected retardation effects, in which case the friction depends cubically on the velocity. Persson and Zhang [117] obtained the formula for friction in the limit of small velocities and finite temperature, again neglecting retardation effects.

In [121, 128], we developed a theory of Casimir friction based on the dynamical modification of the well known Lifshitz theory [42] of the Casimir interaction. In the non-retarded limit and for zero temperature, this theory agrees with the results of Pendry [115]. Similarly, in the non-retarded limit and for small sliding velocity, this theory agrees with the study of Persson and Zhang [117]. The calculation of the Casimir friction is more complicated than that of the Casimir-Lifshitz force (and of the radiative heat transfer), because it requires the determination of the electromagnetic field between moving boundaries. The solution can be found by writing the boundary conditions on the surface of each body in the rest reference frame of this body. The relation between the electromagnetic fields in the different reference frames is determined by the Lorenz transformation. In [121], the electromagnetic field in the vacuum gap between the bodies was calculated to linear order in V/c. These linear terms correspond to the mixing of electromagnetic waves with different polarizations. The waves with different polarization are statistically independent. Thus, after averaging the stress tensor over the fluctuating electromagnetic field, the mixing terms will give a contribution to the friction force in the order of $(V/c)^2$. In [121], the mixing terms were neglected, and the resulting formula for friction force is accurate to order $(V/c)^2$. The same approximation was used in [144] to calculate the frictional drag between quantum wells, and in [99, 100] to calculate the friction force between plane parallel surfaces in normal relative motion. For the case of resonant photon tunneling between surface localized states, normal motion gives drastically different result from parallel relative motion. It was shown that the friction may increase by many orders of magnitude when the surfaces are covered by adsorbates, or can support low-frequency surface plasmons. In this case, the friction is determined by resonant photon tunneling between adsorbate vibrational modes, or surface plasmon modes. When one of the bodies is sufficiently rarefied, this theory gives the friction between a flat surface and a small particle, which, in the non-retarded limit, is in agreement with the results of Tomassone and Widom [145]. A theory of the Casimir friction between a small particle and flat surface, which takes into account screening, non-local optic effects, and retardation effects, was developed in [139]. In [129], the correctness of the approach based on the dynamical modification of the Lifshitz theory was confirmed (at least to linear order in the sliding velocity v) by rigorous quantum mechanical calculations (using the Kubo formula for friction coefficient).

In [128], we presented a fully relativistic theory to the Casimir-Lifshitz forces and the radiative heat transfer at non-equilibrium conditions, when the bodies are at different temperatures, and move relative to each other with an arbitrary velocity v. In comparison with previous calculations [99, 100, 121, 144], we did not make any approximation in the Lorentz transformation of the electromagnetic field. Thus, we determined the field in one inertial reference frame from the field in another reference frame, resulting in an exact solution of the electromagnetic problem. Knowing the electromagnetic field, we calculated the stress tensor and the Poynting vector, which determined the Casimir-Lifshitz forces and the heat transfer, respectively. Upon going to the limit when one of the bodies is rarefied, we obtained the interaction force and the heat transfer for a small particle-surface configuration [150].

Philbin and Leonhardt [122, 123] (henceforth refereed to as PL) calculated the Casimir force and friction due to electromagnetic fluctuations between two perfectly flat parallel dielectric surfaces separated by a vacuum and moving parallel to each other. In [122] PL used Lifshitz theory [42, 43, 107] and considered only the case of zero temperature. The spectral correlation function for a fluctuating electromagnetic field was expressed via the Green function of the electromagnetic field, which was assumed to have the same analytical properties as in the equilibrium case when the relative sliding velocity is zero. The cause of the discrepancy with the previous studies was identified as a failure by PL to correctly account for the modification of the analytic structure for the Green function found in the complex frequency plane when two surfaces are in relative motion [124].

The Lifshitz's theory of the van der Waals-Casimir interaction [42, 43, 107] also includes the effect of thermal radiation. The *Casimir effect* is therefore also taken to describe forces that have a contribution from thermal fluctuations as well as from the quantum fluctuations. The formalism developed by Lifshitz, however, cannot be used for plates at different temperatures. The general case of different temperatures for plates sliding relative to each other was considered in [123, 128].

In [123], PL used the same approach as in [128], which is based on a dynamic modification of the Rytov's theory. The theory presented in [123] contains, as a limiting case, the theory from [122]. For the contributions to the Casimir forces resulting from thermal fluctuations, PL obtained the same results as in [128]. However at zero temperature, PL obtained a result that contradicts a substantial body of earlier results [10, 11, 115, 121, 128]. Their conclusion was that, at zero temperature, where only quantum fluctuations occur, friction is precisely zero. In [126] (see also Appendix F), we argued for the correctness of the earlier results and pointed to the errors in the reasoning of PL.

Silveirinha proposed a theory of quantum friction [146–148], which contradicts a large number of papers devoted to the study of quantum friction, assuming that the fluctuating electromagnetic field created by moving bodies can be described by superposition of eigenmodes. All bodies have fluctuations, which are defined in the rest reference frame of the corresponding body. When bodies are moving relative to each other there is also relative motion of these fluctuations. In the simplest case, these fluctuations can be described by systems of harmonic oscillators. Thus, there may be two systems of harmonic oscillators moving relative to each other. When both systems are at rest there are eigenmodes, but when they are sliding relative to each other, the whole system has no eigenmodes because it is a time dependent problem.

At present, the Casimir friction has been studied in the configurations: plate–plate [11, 99, 100, 115, 116, 121, 128, 149], neutral particle-plate [11, 118–120, 139, 145, 150–156], and neutral particle-blackbody radiation [11, 128, 155, 157–161]. While the predictions of the theory for the Casimir forces were verified in many experiments [89], the detection of the Casimir friction is still a challenging problem for experimentalists. However, the frictional drag between quantum wells [112–114] and graphene sheets [162, 163], and the current–voltage dependence of non-suspended graphene on the surface of the polar dielectric SiO_2 [164], were accurately described using the theory of the Casimir friction [144, 149, 165]. At present frictional drag experiments [112–114, 162–164] have been performed only for weak electric fields, when the induced drift motion of the free carriers is smaller than the threshold velocity for quantum friction. Thus, in these experiments, the frictional drag is dominated by the contributions from thermal fluctuations. However, the measurements of the current–voltage dependence [164] were performed for the high electric field, where the drift velocity is above the threshold velocity, and where the frictional drag is dominated by quantum fluctuations [149, 165]. For reviews of the Casimir friction see [10, 11].

The non-contact friction was investigated for the first time by a non-contact force microscopy setup [19–21]. Thus, Gotsmann and Fuchs [20] reported measurements of a long-range non-contact friction between an aluminum tip and a gold (111) surface. The friction force, F acting on the tip was found to be proportional to the velocity v, $F = \Gamma v$. For motion of the tip normal to the surface the friction coefficient $\Gamma(d) = C \cdot d^{-3}$, where d is the tip-sample spacing and $C = (8.0^{+5.5}_{-4.5}) \times 10^{-35}\,\mathrm{N\,s\,m^2}$. Later Stipe et al. [21] studied non-contact friction between a gold surface and a gold-coated cantilever as a function of tip-sample spacing d, temperature T, and the bias voltage V. For vibration of the tip parallel to the surface they found $\Gamma(d) = \alpha(T)(V^2 + V_0^2)/d^n$, where $n = 1.3 \pm 0.2$, and $V_0 \sim 0.2\,\mathrm{V}$. At 295 K, for the spacing $d = 100$ Å they found $\Gamma = 1.5 \times 10^{-13}\,\mathrm{kgs^{-1}}$, which is ~500 times smaller than that reported in [20] at the same distance using a parallel cantilever configuration. An applied voltage of 1 V resulted in a friction $\Gamma = 3 \times 10^{-12}$ kg/s at 300 K and $d = 20$ nm. Using the fluctuation-dissipation theorem, the force fluctuations were interpreted in terms of near-surface fluctuating electric fields interacting with static surface charge. Recently, Kuehn et al. [24] observed a large non-contact friction over polymer thin films. In [21], the non-contact friction has been also measured for fused silica samples. Near the silica surface, the friction was found to be an order of magnitude larger than for the gold sample. The silica sample had been irradiated with γ rays, which produce E' centers (Si dangling bonds) at a density of $7 \times 10^{17}\,\mathrm{cm^{-3}}$. Although the sample is electrically neutral overall, the E' centers are known to be positively charged, creating enhanced field inhomogeneity and causing the non-contact friction to rise by another order of magnitude.

Kisiel et al. [166] studied non-contact friction on a Nb film across the critical temperature, T_c using a highly sensitive cantilever oscillating in the pendulum geometry in ultrahigh vacuum. The friction coefficient Γ is reduced by a factor of three when the sample enters the superconducting state. The temperature decay of Γ is found to be in good agreement with the Bardeen-Cooper-Schrieffer theory, meaning that friction has an electronic nature in the metallic state, whereas phononic friction dominates in the superconducting state. This is supported by the dependence of friction on the probe-sample distance, d, and on the bias voltage, V Γ is found to be proportional to d^{-1} and V^2 in the metallic state, whereas $\Gamma \sim d^{-4}$ and $\Gamma \sim V^4$ in the superconducting state. Therefore, phononic friction becomes the main dissipation channel below the critical temperature.

Dorofeyev et al. [19] claim that the non-contact friction observed in [19, 20] is due to Ohmic losses mediated by the fluctuating electromagnetic field. This claim is controversial, however, since the Casimir friction for good conductors such as copper has been shown [121, 139, 144, 167] to be many orders of magnitude smaller than the friction observed by Dorofeyev et al. In [168], it was proposed that in comparison with good conductors, the Casimir friction may be strongly enhanced between the high resistivity mica substrate and silica tip. However, in the experiment et al. the mica substrate and silica tip were coated by gold films thick enough to completely screen the electromagnetic interaction between the underlying dielectrics.

At small separation $d \sim 1$ nm, resonant photon tunneling between adsorbate vibrational modes on the tip and the sample may increase the Casimir friction by seven orders of magnitude in comparison with the good conductors with clean surfaces [99, 100]. However, the distance dependence ($\sim 1/d^6$) is stronger than that observed experimentally [21].

In [169], a theory of non-contact friction was suggested where by the friction arises from Ohmic losses associated with the electromagnetic field created by moving charges induced by the bias voltage. In the case of a spherical tip, this theory predicts the same weak distance dependence of the friction as observed in the experiment, but the magnitude of the friction is many orders of magnitude smaller than is found experimentally. In [170, 171], we have shown that the electrostatic friction can be greatly enhanced if there is an incommensurate adsorbate layer that can exhibit acoustic vibrations. This theory gives a tentative explanation for the experimental non-contact friction data [21]. The large non-contact friction observed in [24, 166] over a thin film of Nb can be also explained by the electrostatic friction [166, 172].

Springer

http://www.springer.com/978-3-662-53473-1

Electromagnetic Fluctuations at the Nanoscale
Theory and Applications
Volokitin, A.; Persson, B.
2017, XIII, 425 p. 93 illus., 61 illus. in color., Hardcover
ISBN: 978-3-662-53473-1