Thermodynamics of the Casimir effect

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Abstract. A complete thermodynamic treatment of the Casimir effect is presented. Explicit expressions for the free and the internal energy, the entropy and the pressure are discussed. As an example we consider the Casimir effect with different temperatures between the plates (T) resp. outside of them (T'). For $T' < T$ the pressure of heat radiation can eventually compensate the Casimir force and the total pressure can vanish. We consider both an isothermal and an adiabatic treatment of the interior region. The equilibrium point (vanishing pressure) turns out instable in the isothermal case. In the adiabatic situation we have both an instable and a stable equilibrium point, if T'/T is sufficiently small. Quantitative aspects are briefly discussed.

PACS. 05.90.+m Other topics in statistical physics, thermodynamics, and nonlinear dynamical systems (restricted to new topics in section 05) – 11.10.Wx Finite-temperature field theory – 61.16.Ch Scanning probe microscopy: scanning tunneling, atomic force, scanning optical, magnetic force, etc.

1 Introduction

The Casimir effect [1] is one of the fundamental effects of Quantum Field Theory. It tests the relevance of the zero point energy: two parallel, large conducting plates in a distance a change the vacuum energy of Quantum Electrodynamics in such a way, that a net attractive force between the plates results. Qualitatively, this situation does not change, if the system is at finite temperature. The quantitative corrections for finite temperature [2], finite conductivity [3] and the necessary changes for related problems (*e.g.* for different geometries) [4] are known, and the Casimir force has been experimentally established [5–7]. The thermodynamics for the original setup has been investigated previously [2,8,9]. Here we shall give a somewhat more complete treatment, in which we consider the region between the plates and outside of them separately. This allows for a situation, in which the two regions have different temperatures (outside T', inside T). If we take $T' < T$, the external pressure is reduced in comparison with the standard situation ($T' = T$). Therefore we expect the existence of a certain distance a_0, at which the Casimir attraction is compensated by the net radiation pressure. We shall investigate this (mechanical) equilibrium point and its stability both for an isothermal and an adiabatic treatment of the interior region.

2 Thermodynamic functions

In this section we shall collect and discuss briefly formulae for thermodynamic functions for the original Casimir

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setup. A major part of the results has been found before [8,9] by various methods. In order to make this paper self-contained, we shall indicate briefly a standard procedure for the derivation and list the results. In addition, we shall give numerical details on the functions involved. We consider two parallel, perfectly conducting square plates (side L, distance a, $L > a$), embedded in a large cube (side L) with one of the plates at face and periodic boundary conditions. We shall consider contributions from the volume $L^2 a$ between the plates (suffix int) resp. $L^2(L - a)$ outside of them (suffix ext) separately. In terms of the partition function Z the free energy of a photon gas at temperature T reads

$$F = -\frac{1}{\beta} \ln Z = \sum (G_0(k) + G_\beta(k)) \qquad (1)$$

with

$$G_0(k) = \frac{\hbar c}{2} k, \quad G_\beta(k) = \frac{1}{\beta} \ln\left(1 - \exp\left(-\beta \hbar c k\right)\right). \quad (2)$$

Here $\beta = 1/k_{\mathrm{B}} T$ with Boltzmann's constant k_{B} and $\hbar c k = \hbar c \sqrt{\mathbf{k}^2}$ is the energy of a photon with wave number $\mathbf{k}$. The sum extends on all accessible wave numbers and polarisation states. In order to keep track of ultraviolet divergences, we shall regularize the contribution at temperature zero replacing $k \to k \exp(-\lambda k)$ in G_0 and considering $\lambda \to 0$ at the end. We assume L fixed, but so large, that sums on photon wave numbers can be replaced by corresponding integrals. Then the contributions to the free energy per unit area $\phi = F/L^2$ read.

$$\phi_{\mathrm{ext}} = \frac{(L - a)\pi}{a^3} \int_0^\infty t^2 G\left(\frac{\pi}{a} t\right) \mathrm{d}t, \qquad (3)$$

$$\phi_{\text{int}} = \frac{\pi}{a^2}\left(\frac{1}{2}\int_0^\infty + \sum_{n=1}^\infty \int_n^\infty\right) tG\left(\frac{\pi}{a}t\right)\,\mathrm{d}t. \qquad (4)$$

The integrals can be done analytically. In the results to be listed below we have expanded the result for G_0 in powers of λ and omitted all terms, which vanish for $\lambda \to 0$. For G_β it turned out convenient to use the polylogarithm $\mathcal{L}_n(z) = \sum_{m=1}^\infty z^m/m^n$, which allows even for a calculation of the indefinite integrals and has simple properties (*cf.* Appendix). Further thermodynamic functions can be calculated from ϕ by standard formulae. We shall give results for the entropy

$$\sigma = S/k_{\mathrm{B}}L^2 = \beta^2 \frac{\partial}{\partial\beta}\phi, \qquad (5)$$

the pressure

$$P = -\left(\frac{\mathrm{d}\phi}{\mathrm{d}a}\right)_T \qquad (6)$$

and the internal energy

$$\epsilon = \frac{E}{L^2} = \frac{1}{L^2}(F + TS) = \phi + \frac{1}{\beta}\sigma. \qquad (7)$$

The results are listed in Table 1 in terms of a finite function $g(v)$ to be specified below. The variable v is the dimensionless quantity (*cf.* [8–10])

$$v = \frac{a}{\pi\hbar c\beta} = \frac{ak_{\mathrm{B}}}{\pi\hbar c}T. \qquad (8)$$

The ultraviolet behavior can be discussed without any details on g. Both contributions to σ are finite. The divergent contributions to the pressure cancel in the sum $P_{\text{ext}} + P_{\text{int}}$ and in the difference $P_{\text{ext}}(\beta') - P_{\text{ext}}(\beta)$, which we shall use in the next section. The total free energy $\phi_{\text{ext}} + \phi_{\text{int}}$ contains a divergent constant $\sim L/\lambda^4$, as well as the total internal energy.

Another formula, which can be read off Table 1 without knowledge of g is the relation

$$3\phi + \frac{1}{\beta}\sigma - aP + LP_{\text{ext}} = \frac{12L\hbar c}{\pi^2\lambda^4}, \qquad (9)$$

which can be attributed to the fact, that most of the contributions scale as $b(v)/a^3$ with some function b.

The function $g(v)$ contains an infinite sum, which cannot be performed analytically. Various forms can be found in the literature [8,9]. We shall prefer a representation, which allows for a fast and accurate numerical computation. For this purpose we use the functions (*cf.* Appendix)

$$k(x) = \left(1 - x\frac{\mathrm{d}}{\mathrm{d}x}\right)\sum_{n=1}^\infty \frac{1}{n^3(\exp(nx)-1)}, \quad h(x) = xk'(x).$$
$$(10)$$

For $x > 0$ the sum converges rapidly, k is positive and h is negative. Both functions vanish exponentially for large argument. Two representations of g in terms of k read

$$g(v) = -v^3\left(\frac{1}{2}\zeta(3) + k(1/v)\right), \qquad (11)$$

$$g(v) = \frac{1}{720} - \frac{\pi^4}{45}v^4 - \frac{v}{4\pi^2}\left(\frac{\zeta(3)}{2} + k(4\pi^2 v)\right) \quad (12)$$

with $\zeta(3) = \mathcal{L}_3(1) = 1.2020569\ldots$ The two forms are related by Poisson's sum formula [11]. Taken together, they contain information on the behavior of thermodynamic functions under temperature inversion ($T \to 1/T$) [8,12] (the quantities used in [8] are $\xi = \pi v$, $f(\xi) = \pi^6 v^4/45 + \pi^2 g(v)$).

In order to discuss the behavior of the thermodynamic functions quantitatively, we write

$$\phi = \phi_L(T) + \frac{\pi^2\hbar c}{a^3}f(v), \ \sigma = \sigma_L(T) + \frac{\pi}{a^2}s(v),$$

$$P = \frac{\pi^2\hbar c}{a^4}p(v), \ \epsilon = e_L(T) + \frac{\pi^2\hbar c}{a^3}e(v), \qquad (13)$$

where (ϕ_L, σ_L, e_L) refer to the extensive contributions $\sim L$ from the external cube. The remainders are connected by simple relations. As a consequence of (9) we have

$$3f(v) + vs(v) - p(v) = 0. \qquad (14)$$

Equation (7) amounts to

$$e(v) = f(v) + vs(v). \qquad (15)$$

Therefore only two of the four functions (f, s, p, e) are linearly independent. Explicit forms in terms of g can be read off Table 1. Expressions in terms of $k(x), h(x)$ result by insertion of g. There are two equivalent forms (A, B) for every function corresponding to (11) resp. (12), which are listed in Table 2.

The leading terms for small values of v (*i.e.* at low temperatures) are found from forms (A) neglecting (k, h). This approximation can be used for $v < 0.09$ with errors less than 1%. The asymptotic behaviour at large values of v (*i.e.* at high temperatures) is obtained from forms (B) neglecting (k, h). The corresponding asymptotic approximations for (f, s, p) can be used in a rather large domain. For $v = 0.25$ the errors are $\leq 1\%$ and decrease rapidly with growing v. Form (A) shows, that the entropy vanishes for $T = 0$, *i.e.* Nernst's law is fulfilled. For isentropic processes T tends to a finite value $T(a = 0)$, which is determined by the entropy alone. Form (B) shows, that the entropy becomes constant in the high-temperature limit (Kirchhoff's theorem [10]). It has to be noted, that there is only a rather narrow domain in v, in which the infinite sums (k, h) play a role. In this region the low-temperature behavior of the Casimir force is gradually changed by temperature effects. This domain is realistic [6,7]: for $T = 18$ °C we have $v \approx 0.04a$ (μm). Using the form (10), one can find numerical values in this domain rapidly and with high precision. Results are shown in the plots given in Figure 1 (in which the broken lines correspond to the asymptotic approximations).

3 Different temperatures and equilibrium

As an application we shall now investigate a situation, in which the temperature T between the plates may differ

Table 1.

function	ext contribution	int contribution
ϕ	$(L-a)\,\hbar c\left[\frac{3}{\pi^2\lambda^4} - \frac{\pi^6}{45}\left(\frac{v}{a}\right)^4\right]$	$\hbar c\left[\left(\frac{3a}{\pi^2\lambda^4} + \frac{\pi^2}{a^3}\left(-\frac{1}{720} + g(v)\right)\right)\right]$
σ	$(L-a)\,\frac{4\pi^5}{45}\left(\frac{v}{a}\right)^3$	$-\frac{\pi}{a^2}\,g'(v)$
P	$\hbar c\left[\frac{3}{\pi^2\lambda^4} - \frac{\pi^6}{45}\left(\frac{v}{a}\right)^4\right]$	$\hbar c\left[-\frac{3}{\pi^2\lambda^4} + \frac{\pi^2}{a^4}\left(-\frac{1}{240} + 3g(v) - vg'(v)\right)\right]$
ϵ	$(L-a)\hbar c\left[\frac{3}{\pi^2\lambda^4} + \frac{3\pi^6}{45}\left(\frac{v}{a}\right)^4\right]$	$\hbar c\left[\frac{3a}{\pi^2\lambda^4} + \frac{\pi^2}{a^3}\left(-\frac{1}{720} + g(v) - vg'(v)\right)\right]$

Table 2.

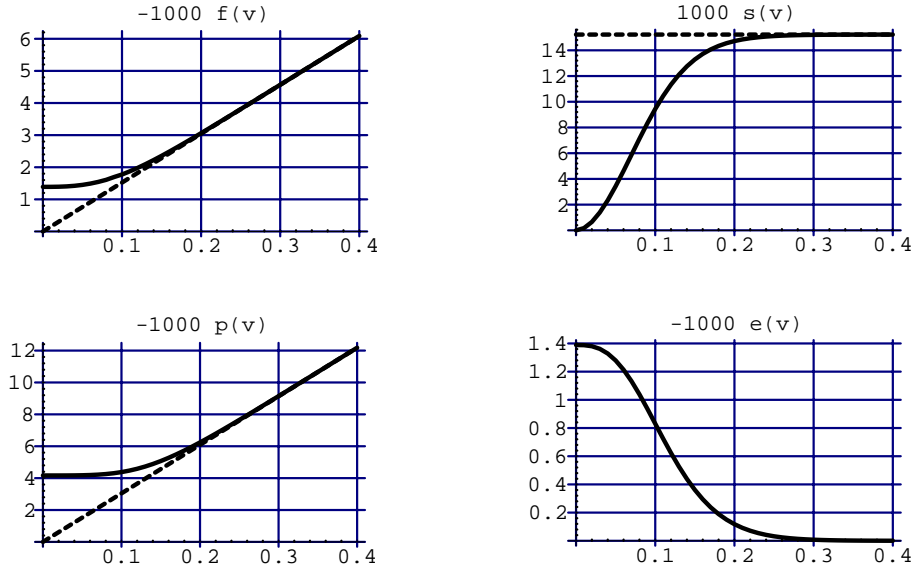| funct.	form (A)	form (B)
f	$-\frac{1}{720} - v^3\left(\frac{\zeta(3)}{2} - \frac{\pi^4}{45}v + k(1/v)\right)$	$-\frac{1}{4\pi^2}v\left(\frac{\zeta(3)}{2} + k(4\pi^2 v)\right)$
s	$v^2\left(\frac{3\zeta(3)}{2} - \frac{4\pi^4}{45}v + 3k(1/v) - h(1/v)\right)$	$\frac{1}{4\pi^2}\left(\frac{\zeta(3)}{2} + k(4\pi^2 v) + h(4\pi^2 v)\right)$
p	$-\frac{1}{240} - v^3\left(\frac{\pi^4}{45}v + h(1/v)\right)$	$-\frac{1}{4\pi^2}v\left(\zeta(3) + 2k(4\pi^2 v) - h(4\pi^2 v)\right)$
e	$-\frac{1}{720} + v^3\left(\zeta(3) - \frac{3\pi^4}{45}v + 2k(1/v) - h(1/v)\right)$	$\frac{1}{4\pi^2}vh(4\pi^2 v)$

Fig. 1. Thermodynamic functions.

from the temperature T' of the exterior region. We shall keep T' resp. $v' = ak_\mathrm{B}T'/\pi\hbar c$ fixed. For the interior region we consider two possibilities. In the first case also T resp. v is kept fixed (isothermal situation). In the second case we treat the internal region as a closed system, so that the entropy σ_int remains constant (adiabatic situation) and T resp. v vary appropriately with a. In both cases we shall focus attention on the question, whether there is a distance a_0, at which the total pressure vanishes. If one of the two plates is movable, the distance $a = a_0$ would constitute mechanical equilibrium between the Casimir attraction and the thermal radiation pressure (which repels the plates). We shall also consider the question, whether this equilibrium is stable.

For an appropriate treatment we consider the quantity

$$P(a, v, v') = P_\mathrm{ext}(T') + P_\mathrm{int}(T) = P_\mathrm{ext}(T') - P_\mathrm{ext}(T)$$
$$+P_\mathrm{ext}(T) + P_\mathrm{int}(T) = \frac{\pi^6\hbar c}{45a^4}G(v, v') \quad (16)$$

(the second form shows, that the divergent contributions are absent, *viz.* Tab. 1) with

$$G(v, v') = v^4 + \frac{45}{\pi^4}p(v) - v'^4 \quad (17)$$

in terms of p from Section 2. We shall always use the form (B) from Table 2. The equilibrium condition

$$P(a, v, v')|_{a=a_0} = 0 \quad (18)$$

amounts to

$$G(v, v')|_{a=a_0} = 0. \tag{19}$$

Solutions are only possible, if $v' < v(a)$, since p is negative. A Taylor expansion of P near $a = a_0$ shows, that dP/da at equilibrium must be negative for a stable situation. Differentiating (16) and using (19), one observes, that the stability condition amounts to

$$\left.\frac{dG(v, v')}{da}\right|_{a=a_0} < 0. \tag{20}$$

We shall always seek solutions considering a scaled form of (19)

$$\kappa^4 = R(v), \quad R(v) = \frac{1}{v_0^4}\left(v^4 + \frac{45}{\pi^4}p(v)\right), \quad \kappa = \frac{v'}{v_0} \tag{21}$$

with some scale v_0.

In the *isothermal* case v is proportional to a. If we take $v_0 = v$, the ratio $\kappa = T'/T$ does not depend on a. From the plot for $p(v)$ given in Figure 1 we can see, that $R(v)$ is a monotonous function with positive tangent. The function is positive above a certain value of v. For any given value of $0 \leq \kappa \leq 1$ we have therefore one solution, which is unstable. Some numerical results are listed in Table 3. The third row gives the distances for $T = 18\ °C$ in μm. The last row is obtained using the asymptotic approximation $p_{as} = -v\zeta(3)/4\pi^2$, which turns out quite accurate.

In the *adiabatic* case we have to evaluate (21) along an isentrope, which corresponds to a curve $\sigma_{int}(v) = const$. A convenient parametrisation is obtained using the constant

$$t^2 = \frac{2\sigma_{int}}{3\pi\zeta(3)} \tag{22}$$

instead of σ_{int}. An equation for the isentrope is obtained inserting the explicit expression for $\sigma_{int}(v) = -\pi g'(v)/a^2$ from Section 2. In terms of t and s the equation reads

$$a^2 t^2 = \frac{2}{3\zeta(3)}\left(s(v) + \frac{4\pi^4}{45}v^3\right). \tag{23}$$

The leading term on the r.h.s. for small v is v^2 (see Tab. 2, form (A)). Therefore the isentrope becomes an isotherme for small v and t can be identified as

$$t = \frac{k_B}{\pi\hbar c}T(a = 0). \tag{24}$$

In order to obtain an explicit form for the isentrope we have to solve (23) for $v = v(at)$. This can be done numerically with high precision. We have used the form (B) from Table 2 for $s(v)$ to determine $v(at)$. The result is plotted in the left diagram of Figure 2. An approximate form $v_{as}(at)$ is obtained neglecting $k + h$ in $s(v)$. The result is

$$v_{as}(at) = \left(B(12\pi^2 a^2 t^2 - 1)\right)^{1/3}, \quad B = \frac{45\zeta(3)}{32\pi^6}. \tag{25}$$

v can be approximated by v_{as} for $at \geq 0.25$ with an error $\leq 0.1\%$. With increasing at the error decreases rapidly.

The right diagram of Figure 2 (in which the broken line corresponds to v_{as}) illustrates this fact.

If we take $v_0 = at$ in (21), the ratio $\kappa(0) = T'/T(a = 0)$ does not depend on a and can therefore be used as an input for (21). The function $R(v)$ shows, however, a different behavior than in the isothermal case. It vanishes for $at = 0.2763$, assumes a maximum at $at = at_M = 0.4391$ and falls off slowly for larger argument (see Fig. 3).

Therefore we obtain no solution, if $\kappa(0)$ is larger than $\kappa_M = (R(at_M))^{1/4} = 0.68542$. For $\kappa < \kappa_M$ there are two solutions: one of them (corresponding to the lower value of at) is unstable, the other one is stable. The distance between the two solutions increases with decreasing $\kappa(0)$. Some numerical results are listed in Table 4. The entries for $a(18\ °C)$ refer to $T(0) = 18\ °C$.

It is observed, that $\kappa(a)$ is close to 1 for the stable equilibrium points. This is due to the slow falloff of $R(v)$. Using the asymptotic approximation $p \to -v_{as}(at)\zeta(3)/4\pi^2$, the data in Table 4 are reproduced with rather small errors.

The existence of stable equilibrium points implies, that a movable plate may perform oscillations about these points. In order to approach the problem of an observation, we shall discuss briefly some quantitative details. For these, we have used the formula for the Casimir pressure

$$\frac{\pi^2\hbar c}{240 a^4} = 1.3001 \times 10^{-7}\frac{N}{cm^2}. \tag{26}$$

Here a is measured in microns (μm). We assume the movable plate situated at the distance a_1 from a stable equilibrium point a, where a_1/a is small enough, so that a linear approximation is possible. For the data in Table 4 (stable points, $18\ °C$) we obtain a restoring force/area of

$$\frac{a_1}{a}(0.39\ldots 28)\frac{pN}{cm^2}. \tag{27}$$

The oscillation frequency is

$$\nu = \frac{1}{\sqrt{m}}(0.12\ldots 6.7) \times 10^{-3}\ Hz. \tag{28}$$

Here m is the mass per area of the movable plate measured in g/cm^2. Thus it seems impossible to observe even one entire oscillation, because the temperature relaxation takes less time. At higher temperatures the situation is slightly improved. At $245\ °C$ the force is 10 times and the frequency 4.2 times larger.

4 Conclusions and outlook

In order to discuss thermal effects, we have considered the standard setup for the Casimir force: two parallel, conducting square plates (side L) in a distance a. The plates are enclosed in a cube $L \times L \times L$ with one plate at face. An ensemble of free photons fufilling boundary conditions at the plates resp. faces was investigated.

In Section 2 we have used Quantum Statistical Mechanics to compute the (free energy, entropy, internal energy) per area L^2 and the pressure. We have calculated
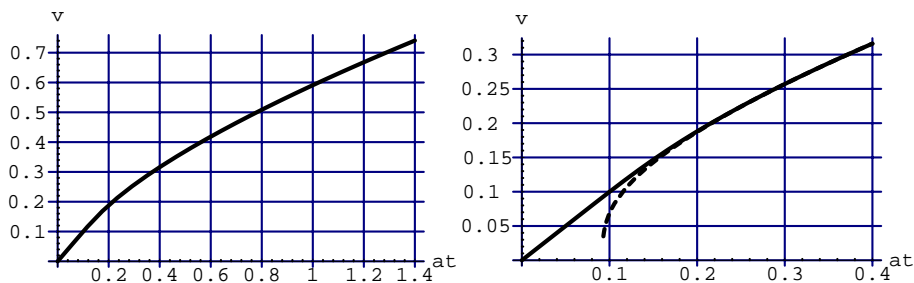
Fig. 2. Isentrope.

Table 3. Isothermal equilibrium.

κ	0	0.2	0.4	0.6	0.8	0.95
$v(a)$	0.2419	0.2421	0.24340	0.2532	0.2879	0.4233
$a(18\ °\mathrm{C})/\mu\mathrm{m}$	5.981	5.984	6.032	6.260	7.117	10.46
$v_{\mathrm{as}}(a)$	0.2414	0.2415	0.2435	0.2528	0.2877	0.4233

Table 4. Adiabatic equilibrium.

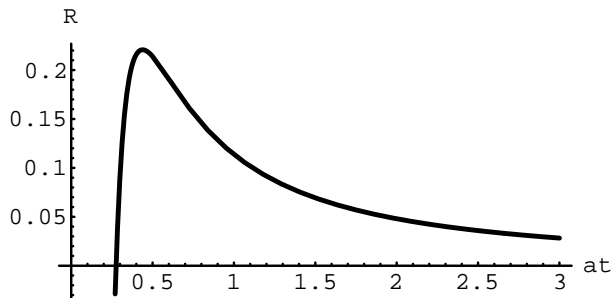|	$\kappa(0)$	0.2	0.4	0.6	0.65
unstab.	at	0.2767	0.2819	0.3148	0.3441
	$a(18\ °\mathrm{C})/\mu\mathrm{m}$	6.839	6.969	7.783	8.506
	$\kappa(a)$	0.2285	0.4592	0.7093	0.7876
stab.	at	26.03	3.235	0.8917	0.6503
	$a(18\ °\mathrm{C})/\mu\mathrm{m}$	643.4	79.98	22.05	16.08
	$\kappa(a)$	0.99998	0.9984	0.9778	0.9565

Fig. 3. Adiabatic equilibrium function R.

the contributions from the space between the plates resp. outside of them separately.

In order to keep track of ultraviolet divergences, a standard regularisation was used. The divergences are absent both in the entropy and in the total pressure. They survive both in the free and internal energy in the extensive contribution from the external cube (*cf.* Tab. 1).

Separating all extensive contributions, the remainders can be written as products of a factor containing some power of a and a function of a dimensionless variable (8) (*cf.* (13)). These four functions are related by two linear equations, of which one (15) is well-known from thermodynamics. The other one (14) is a consequence of scaling

properties. Both formulae (Tab. 2) and diagrams (Fig. 1) for the functions are presented. The results allow for accurate quantitative information, also in the (relatively narrow) domain between the behavior at low resp. high temperatures.

In Section 3 we have considered a situation with different temperatures between (T) resp. outside (T') of the plates. For $T > T'$ the Casimir pressure is reduced by thermal effects and at some distance a the total pressure can vanish, so that the regions inside resp. outside the plates are in mechanical equilibrium. If both T and T' are fixed (isothermal case), this equilibrium has turned out unstable. If only T' is fixed and T is allowed to vary with a in such a way, that the entropy between the plates remains constant (adiabatic case), we have found also a region with stable equilibrium, if $T'/T(a = 0)$ is small enough. The frequency of oscillations of one plate about stable equilibrium distances turned out too low for an observation (*cf.* (28)). Whether the (very small) restoring force (*cf.* (27)) can be measured, must be left open.

It is known [4], that the Casimir force depends on the geometry of the setup. Accurate experimental results [6,7] have so far been obtained only for a setup consisting of a plate and a sphere. Temperature effects have been observed, but only the low temperature behavior was involved. An experiment with the original setup (as studied

here), carried out at larger distances, would test the theory in a different domain.

Appendix A

Here we shall give a collection of formulae for the polylogarithm $\mathcal{L}$, which we have used in computations. Some of these are also useful in Quantum Statistical Mechanics of ideal Bose gasses with other constituents than photons.

Let r, s be integers and $0 \leq y \leq 1$. The polylogarithm $\mathcal{L}_r(y)$ can be defined by the series

$$\mathcal{L}_r(y) = \sum_{n=1}^{\infty} \frac{y^n}{n^r} \qquad (A.1)$$

and fulfills evidently the relations

$$\mathcal{L}_r(0) = 0, \quad \mathcal{L}_r(1) = \zeta(r), \quad \mathcal{L}_r(y) \geq 0. \qquad (A.2)$$

By differentiation we obtain

$$y\frac{\mathrm{d}}{\mathrm{d}y}\mathcal{L}_r(y) = \mathcal{L}_{r-1}(y), \qquad (A.3)$$

$$\int \mathcal{L}_r(y)\frac{\mathrm{d}y}{y} = \mathcal{L}_{r+1}. \qquad (A.4)$$

For $r \leq 1$ the function is elementary. We have

$$\mathcal{L}_1(y) = -\ln(1 - y), \qquad (A.5)$$

$$\mathcal{L}_0(y) = \frac{y}{1 - y}. \qquad (A.6)$$

Putting $y = \exp(-z)$, we obtain from (A.3)

$$\left(\frac{\mathrm{d}}{\mathrm{d}z}\right)^s \mathcal{L}_r(\exp(-z)) = (-1)^s \mathcal{L}_{r-s}(\exp(-z)). \qquad (A.7)$$

From (A.4) we obtain

$$\int \mathcal{L}_r(\exp(-z))\mathrm{d}z = -\mathcal{L}_{r+1}(\exp(-z)). \qquad (A.8)$$

Combining (A.7) and (A.8) and using repeated partial integration, we obtain

$$\int z^s \mathcal{L}_r(\exp(-z))\mathrm{d}z = -s! \sum_{n=0}^{s} \frac{z^{s-n}}{(s-n)!}\mathcal{L}_{r+n+1}(\exp(-z)). \qquad (A.9)$$

With $r = 1$ this formula can be used for the evaluation of the integrals on G_β in (3, 4).

For partition functions we have to put $z = nx$ and to evaluate infinite sums on n. A useful formula reads

$$\sum_{n=1}^{\infty} \mathcal{L}_r(\exp(-nx)) = \sum_{n=1}^{\infty} \frac{1}{n^r}\frac{1}{\exp(nx) - 1}. \qquad (A.10)$$

The second form is obtained from the first one using the definition of the polylogarithm and summing the resulting geometrical series. It is noted, that the second form converges exponentially (also for negative r), as long as $x > 0$. For an approximate evaluation the series can be terminated, if x is large enough.

The functions (10) can be obtained starting from (A.10) with $r = 1$:

$$j(x) = \sum_{n=1}^{\infty} \frac{1}{n^3 N}, \quad N = \exp(nx) - 1 > 0. \qquad (A.11)$$

Carrying out the derivatives, we obtain

$$k(x) = (1 - x\frac{\mathrm{d}}{\mathrm{d}x})j(x)$$
$$= \sum_{n=1}^{\infty} \frac{1}{n^3}\left(\frac{1 + nx}{N} + \frac{nx}{N^2}\right) > 0, \qquad (A.12)$$

$$h(x) = -x^2 \sum_{n=1}^{\infty} \frac{1}{n}\left(\frac{1}{N} + \frac{3}{N^2} + \frac{2}{N^3}\right) < 0. \qquad (A.13)$$

These forms have been used in all numerical calculations.

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