PHYSICAL REVIEW A VOLUME 11, NUMBER 5 MAY 1975

Temperature dependence of Van der Waals forces in classical electrodynamics with classical electromagnetic zero-point radiation*

Timothy H. Boyer

Department of Physics, City College of the City University of New York, New York, New York 10031

(Received 28 August 1974)

Retarded dispersion forces are calculated at finite temperature in the theory of classical electrodynamics with classical electromagnetic zero-point radiation. Expressions are given at all separations for the forces between a polarizable particle and a conducting wall and between two polarizable particles where the particles are represented by electric dipole oscillators immersed in thermal radiation. Also given are the simple expressions holding in the unretarded short-distance limit, and in the asymptotic large-distance limit. At any finite nonzero temperature T, the asymptotic large-distance Van der Waals force between two polarizable particles separated by a distance $R \gg \hbar c/KT$ is given by the potential $U(R) = -3\alpha^2 KT/R^6$ rather than the Casimir-Polder form for zero temperature, $U(R) = -(23/4\pi)\alpha^2\hbar c/R^7$, where α is the static polarizability of each particle. Also the R^{-6} form holds at high temperatures for any fixed separation. The finite-temperature analysis presented follows directly from earlier classical work at zero temperature since within the classical theory, classical zero-point radiation and classical thermal radiation are treated on the same footing. The classical calculations are easier than those of quantum-electrodynamic perturbation theory but have been shown generally to reproduce the quantum results for dipole-oscillator systems. The forces in the high-temperature limit are shown to agree with the results of classical statistical mechanics and with the use of the Rayleigh-Jeans law for the thermal radiation spectrum. The new results for polarizable particles fit nicely with earlier work by other authors on the finite-temperature corrections to the Casimir effect, the force between uncharged conducting parallel plates. It is emphasized that the force between conducting plates may be regarded as due to the classical boundary conditions at the conductors rather than to any discrete quantum aspects; the Rayleigh-Jeans spectrum also leads to a force between conducting plates and this force is in agreement with the high-temperature limit of previous calculations including zero-point radiation.

I. INTRODUCTION

In this paper we will analyze the finite-temperature corrections to Van der Waals forces between polarizable particles represented in the Drude-Lorentz approximation as harmonic electric dipole oscillators immersed in thermal radiation. The results suggest interesting changes in the asymptotic form of Van der Waals forces at large distances and high temperatures. Also the work indicates the agreement of the forces at high temperature with the results of traditional classical statistical mechanics. The paper represents another calculation within the theory of classical electrodynamics with classical electromagnetic zero-point radiation.

There has been continuing interest[1] in Van der Waals forces in both theoretical and experimental physics. In some theoretical work[2] the motivation involves the demonstration of the variety of calculational techniques available for electromagnetic interactions. However, in other cases there is direct connection with ongoing experimental work[3] and application to chemical and biological problems.[4]

Most calculations of the dispersion forces between neutral polarizable systems have been carried out for the absolute zero of temperature. The exceptions involve finite-temperature analysis[5] of the Casimir effect[6] involving the attraction between two uncharged conducting parallel plates, and of Lifshitz's extension[7] of Casimir's investigation to the forces between dielectric materials. In the experimental work involving forces between macroscopic plates at room temperature, the finite temperature effects are at the edge of observation. There has been little attention given to finite temperature corrections to forces between molecules, probably because they are anticipated to be unimportant in current room-temperature experimental work, and also perhaps because of the more complicated sums over excited states required within quantum perturbation calculations.

In work published recently, Van der Waals forces have been calculated within classical electrodynamics including classical electromagnetic zero-point radiation.[8-11] In this work the polarizable particles are represented as electric dipole harmonic oscillators. It has been shown that for such nonrelativistic oscillators coupled to the full radiation field, the problem can be solved exactly in both classical[10] and quantum[12] electrodynamics; moreover, at any temperature, the average values of products of classical variables agree exactly with the expectation values of the *symmetrized* products of the corresponding quantum electrodynamic operators.[13] In particular, the energies calculated in the two theories agree because the quantum Hamiltonian is a symmetrized operator form. Because of this demonstrated general agreement between the classical and quantum results for harmonic oscillator systems, it seems well worthwhile providing the results for the temperature dependence of Van der Waals forces in classical electrodynamics with classical electromagnetic zero-point radiation. The classical calculations are incomparably easier than those of quantum electrodynamic perturbation theory. Furthermore, the classical theory provides an immediate physical picture for understanding the temperature dependence of the forces.

II. RETARDED DISPERSION FORCES AT ALL DISTANCES FOR FINITE TEMPERATURE

A. Classical theory with zero-point radiation

In the work to follow, we consider atoms or molecules in the Drude-Lorentz approximations as classical electric dipole oscillators with natural frequency ω_0. The frequency ω_0 is chosen so that $\hbar\omega_0$ corresponds to the energy separation between the ground state and first excited P state of the quantum description. We then apply classical electrodynamics in all our calculations.

The theory of classical electrodynamics with classical electromagnetic zero-point radiation is a classical electron theory which chooses the retarded Green's function in solving Maxwell's equations but chooses the homogeneous solution of Maxwell's equations to correspond to random fluctuating radiation with a Lorentz-invariant spectrum.[14,15] If one chooses the one undetermined constant setting the scale of the random radiation at temperature $T=0$ so as to give a free-field energy $\frac{1}{2}\hbar\omega$ per normal mode, the theory yields a number of results in agreement with quantum theory and with experiment.[16]

B. Mechanism for Van der Waals forces

In the theory of classical electrodynamics with classical electromagnetic zero-point radiation, the mechanism for Van der Waals forces is immediately apparent. The random fluctuating radiation drives the polarizable particles into random oscillation. The radiation emitted by the two particles is correlated with the initial random radiation in such a way as to lead to a nonvanishing average for the classical Lorentz force on each particle. The classical force is precisely the Van der Waals force between the particles.

In earlier work[10] it was shown how this physical picture involving fluctuations at zero temperature can be carried through quantitatively, yielding exactly the quantum theoretical results for the retarded Van der Waals forces at all distances. Now within the classical theory presented here, there is no qualitative difference between the random classical radiation at zero temperature and at finite nonzero temperature. Both involve random classical radiation; the only change is in the spectrum of the radiation. Indeed it has been shown that the presence of classical zero-point radiation at zero temperature leads naturally within classical theory to Planck's spectrum for the random thermal radiation at finite temperature.[15] Hence, in order to convert our earlier results to expressions holding at finite temperature, we merely insert Planck's spectrum into the random radiation expression where we formerly had the zero-point spectrum.

This classical point of view which treats thermal radiation on exactly the same level as zero-point radiation is quite different from the conventional photon picture used within much of contemporary thinking. Nevertheless, it has been shown quite generally[13] that despite the enormous difference in point of view, the average values obtained in the classical theory of nonrelativistic electric dipole oscillators coupled to thermal radiation including zero-point radiation are precisely the same as the expectation values of *symmetrized* products of quantum operators in quantum electrodynamics. The quantum operators corresponding to physical observables, such as the energy, are usually chosen as symmetrized expressions of the basic field, position and momentum operators. Hence the quantum calculations are expected to agree with the classical results obtained here.

C. General expressions for forces at finite temperature

The derivation of the retarded Van der Waals forces at all distances was given recently[10] within classical electrodynamics with classical electromagnetic zero-point radiation. The derivation assumed a random electromagnetic field in free space given by a superposition of plane waves [Eq. (1), Ref. 11],

$$\vec{E}_{ZP}(\vec{r},t)=\mathrm{Re}\sum_{\lambda=1}^{2}\int d^3k\,\hat{\epsilon}(\vec{k},\lambda)\mathfrak{h}(\vec{k},\lambda)\times\exp\{i[\vec{k}\cdot\vec{r}-\omega t+\theta(\vec{k},\lambda)]\}\ , \tag{1}$$

$$\hat{\epsilon}(\vec{k},\lambda)\cdot\hat{\epsilon}(\vec{k},\lambda')=\delta_{\lambda\lambda'}\ , \tag{2}$$

$$\vec{k}\cdot\hat{\epsilon}(\vec{k},\lambda)=0,\quad \omega=ck\ , \tag{3}$$

and with the scale of the spectrum set by Planck's constant,

$$\pi^2 \mathfrak{h}^2(\vec{k}, \lambda) = \tfrac{1}{2}\hbar\omega \quad . \tag{4}$$

In the present work we merely replace this spectrum of classical zero-point radiation by the Planck spectrum at finite temperature,

$$\pi^2 \mathfrak{h}^2(\vec{k}, \lambda, T) = \frac{\hbar\omega}{\exp(\hbar\omega/KT) - 1} + \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar\omega \coth(\hbar\omega/2KT) \quad . \tag{5}$$

All of the calculations go through exactly as in Ref. 10. The finite-temperature spectrum (5) is substituted in the final evaluation of $\mathfrak{h}$. In effect, the potential expansions change by the insertion of a factor of $\coth(\hbar\omega/2KT)$. Thus the result for the Van der Waals force between an electrically polarizable particle and a conducting wall separated by a distance R chosen along the z axis [Eqs. (42)–(44), Ref. 10] becomes at finite temperature:

$$F_{PWz} = -\frac{\partial}{\partial R} U_{PW}(R) \ , \tag{6}$$

$$U_{PW}(R) = \frac{\hbar c}{2\pi} \int_{k=0}^{\infty} dk \coth\left(\frac{\hbar\omega}{2KT}\right) \times \mathrm{Im}\ln\left[\left(1+\frac{\Sigma_x}{C}\right)\left(1+\frac{\Sigma_y}{C}\right)\left(1+\frac{\Sigma_z}{C}\right)\right] \ . \tag{7}$$

The notation is that of Ref. 10. Also, the force between two electrically polarizable particles separated by a distance R chosen along the z axis [Eq. (80), (81), Ref. 10] becomes

$$F_{2Pz} = -\frac{\partial}{\partial R} U_{2P}(R) \ , \tag{8}$$

$$U_{2P}(R) = \frac{\hbar c}{2\pi} \int_{k=0}^{\infty} dk \coth\left(\frac{\hbar\omega}{2KT}\right) \times \mathrm{Im}\ln\left[\left(1-\frac{\eta_x^2}{C^2}\right)\left(1-\frac{\eta_y^2}{C^2}\right)\left(1-\frac{\eta_z^2}{C^2}\right)\right] \ . \tag{9}$$

The general calculation has now been completed; the results given here are exact and can be used as the basis for numerical calculations. However, many readers will presumably gain little enlightenment from these elegant mathematical forms. In an effort to reveal some of the physical character of the forces, we will specialize the general expressions to two separate limiting cases. When the separations R involved are small, the retardation effects become unimportant and we may deal with unretarded London–Van der Waals forces. In the opposite limit of large separations R, we are involved with asymptotic retarded Van der Waals forces. The simple forms taken by the potentials in these two limiting cases will be discussed separately.

III. UNRETARDED LONDON–VAN DER WAALS FORCES

A. Approximations for small separations

The secular fluctuations of the polarizable particles are characterized by the oscillator frequency ω_0. When the separation R is small compared to ω_0,

$$\omega_0 R/c \ll 1 \ , \tag{10}$$

then the approximation for unretarded forces is available.

In order to introduce the approximations, we have found it convenient to work with the forces, rather than the potentials, as given in Eqs. (6) and (8). We carry out the derivative with respect to R and so obtain for the particle-wall case [see Eq. (39) of Ref. 10],

$$F_{PW} = F_{PW}^{(x)} + F_{PW}^{(y)} + F_{PW}^{(z)} \ , \tag{11}$$

$$F_{PW}^{(x)} = -\pi\int_{\omega=0}^{\infty} d\omega \frac{\mathfrak{h}^2}{\omega} \times\left[\frac{1}{|C+\Sigma_x|^2}\left(\mathrm{Re}\,(C^* + \Sigma_x^*)\frac{\partial}{\partial R}\,\mathrm{Im}\Sigma_x - \mathrm{Im}(C+\Sigma_x)\frac{\partial}{\partial R}\,\mathrm{Re}\Sigma_x^*\right)\right] , \tag{12}$$

with analogous expressions for $F_{PW}^{(y)}$ and $F_{PW}^{(z)}$. In the case of two polarizable particles [see Eq. (78) of Ref. 10],

$$F_{2P} = F_{2P}^{(x)} + F_{2P}^{(y)} + F_{2P}^{(z)} \ , \tag{13}$$

$$F_{2P}^{(x)} = -\pi\int_{\omega=0}^{\infty} d\omega \frac{\mathfrak{h}^2}{\omega}\left[\frac{1}{|C+\eta_x|^2}\left(\mathrm{Re}(C^* + \eta_x^*)\frac{\partial}{\partial R}\,\mathrm{Im}\eta_x - \mathrm{Im}(C+\eta_x)\frac{\partial}{\partial R}\,\mathrm{Re}\eta_x^*\right) - \frac{1}{|C-\eta_x|^2}\left(\mathrm{Re}(C^* - \eta_x^*)\frac{\partial}{\partial R}\,\mathrm{Im}\eta_x - \mathrm{Im}(C-\eta_x)\frac{\partial}{\partial R}\,\mathrm{Re}\eta_x^*\right)\right] \ . \tag{14}$$

The symbol C in the equations stands for

$$C=-\omega^2+\omega_0^2-i\Gamma\omega^3\ , \tag{15}$$

with

$$\Gamma=\tfrac{2}{3}e^2/mc^3\ , \tag{16}$$

for a harmonic oscillator of charge e, mass m, and frequency ω_0. Also, the symbols Σ_x, Σ_y, Σ_z are given by [see Eqs. (14), (15) of Ref. 10],

$$\Sigma_x=\Sigma_y=+\tfrac{3}{2}\Gamma\omega^3\left(\frac{1}{2kR}+\frac{i}{(2kR)^2}-\frac{1}{(2kR)^3}\right)\times\exp(i2kR)\ , \tag{17}$$

$$\Sigma_z=-\tfrac{3}{2}\Gamma\omega^3 2\left(\frac{-i}{(2kR)^2}+\frac{1}{(2kR)^3}\right)\exp(i2kR)\ , \tag{18}$$

while those for η_x, η_y, η_z are of the form [see Eqs. (54), (55) of Ref. 10],

$$\eta_x=\eta_y=-\tfrac{3}{2}\Gamma\omega^3\left(\frac{1}{kR}+\frac{i}{(kR)^2}-\frac{1}{(kR)^3}\right)\exp(ikR)\ , \tag{19}$$

$$\eta_z=-\tfrac{3}{2}\Gamma\omega^3 2\left(\frac{-i}{(kR)^2}+\frac{1}{(kR)^3}\right)\exp(ikR)\ . \tag{20}$$

Now the damping time Γ is regarded as very small compared to the period of oscillation $2\pi/\omega_0$. For electrons $\Gamma\sim 6\times 10^{-24}$ sec. Thus the integrands in Eqs. (12) and (14) have resonant denominators $|C+\Sigma_x|^2$, $|C+\eta_x|^2$, and $|C-\eta_x|^2$ for ω near ω_0. At these frequencies $\omega\sim\omega_0$, the condition (10) of small separation leads to

$$\exp(ikR)\cong 1+ikR,\qquad (kR)^{-3}\gg(kR)^{-2}\gg(kR)^{-1}\ , \tag{21}$$

and so to the approximations

$$\Sigma_x=\Sigma_y\cong-\frac{3}{2}\frac{\Gamma\omega^3}{(2kR)^3}\,(1+i2kR)\ , \tag{22}$$

$$\Sigma_z\cong-\frac{3}{2}\frac{\Gamma\omega^3 2}{(2kR)^3}\,(1+i2kR)\ , \tag{23}$$

$$\eta_x=\eta_y\cong+\frac{3}{2}\frac{\Gamma\omega^3}{(kR)^3}\,(1+ikR)\ , \tag{24}$$

$$\eta_z\cong-\frac{3}{2}\frac{\Gamma\omega^3 2}{(kR)^3}(1+ikR)\ . \tag{25}$$

B. Resonance-force calculations for particle-wall case

The calculations for the unretarded forces are now completed by the traditional method for the resonant contributions at ω_Σ in Eq. (12), and at ω_+ and ω_- in Eq. (14) where

$$\omega_\Sigma^2=\omega_0^2+\mathrm{Re}\Sigma_x\ , \tag{26}$$

$$\omega_+^2=\omega_0^2+\mathrm{Re}\eta_x\ , \tag{27}$$

$$\omega_-^2=\omega_0^2-\mathrm{Re}\eta_x\ . \tag{28}$$

All expressions in the integrands which do not involve $\omega-\omega_{\mathrm{res}}$ where ω_{res} is the frequency of resonance of the denominator are replaced by ω_{res}. The lower limit of integration is extended to $-\infty$. For example,

$$F_{PW}^{(x)}=-\pi\left[\frac{\mathfrak{h}^2}{\omega}\left(0-(-\Gamma\omega^3+\mathrm{Im}\Sigma_x)\frac{\partial}{\partial R}\mathrm{Re}\Sigma_x^*\right)\right]_{\omega=\omega_\Sigma}\times\int_{-\infty}^{\infty}d\omega\,\frac{1}{(2\omega_\Sigma)^2(\omega-\omega_\Sigma)^2+(-\Gamma\omega^3+\mathrm{Im}\Sigma_x)_{\omega=\omega_\Sigma}}$$

$$=-\pi\left(\frac{\mathfrak{h}^2}{\omega}\frac{\partial}{\partial R}\mathrm{Re}\Sigma_x^*\right)_{\omega=\omega_\Sigma}\frac{\pi}{2\omega_\Sigma}\ . \tag{29}$$

In this result, we may approximate $\omega_\Sigma\sim\omega_0$. Introducing the approximate value for $\mathrm{Re}\Sigma_x$ in (22) and the spectral function $\mathfrak{h}^2$ from (5), we obtain

$$F_{PW}^{(x)}=-\frac{3}{32}\left(\frac{e^2}{m\omega_0^2}\right)\frac{\hbar\omega_0}{R^4}\coth\left(\frac{\hbar\omega_0}{2KT}\right)\ . \tag{30}$$

The contributions for $F_{PW}^{(y)}$ and $F_{PW}^{(z)}$ are found analogously. Thus the unretarded force between a polarizable particle and a conducting wall is

$$F_{PW}=-\frac{3}{8}\frac{\alpha\hbar\omega_0}{R^4}\coth\left(\frac{\hbar\omega_0}{2KT}\right) \tag{31}$$

or

$$F_{PW}=-\frac{\partial}{\partial R}U_{PW}(R)\ , \tag{32}$$

$$U_{PW}(R)=-\frac{\alpha\hbar\omega_0}{8R^3}\coth\left(\frac{\hbar\omega_0}{2KT}\right)\ , \tag{33}$$

where

$$\alpha=e^2/m\omega_0^2 \tag{34}$$

is the static electric polarizability of the oscillator. Except for the factor of $\coth(\hbar\omega_0/2KT)$, this is the same as the zero-temperature result of Eqs. (33) and (25) in Ref. 6 obtained from a different mathematical procedure.

C. Resonant calculation for two particles

The force between two polarizable particles is obtained in basically the same manner. Here we obtain two resonant contributions from (14),

$$F_{2P}^{(x)} = -\pi\left\{\left[\frac{\mathfrak{h}}{\omega}\left(0-(-\Gamma\omega^3+\mathrm{Im}\eta_x)\frac{\partial}{\partial R}\mathrm{Re}\eta_x^*\right)\right]_{\omega=\omega_+}\int_{-\infty}^{\infty}d\omega\frac{1}{(2\omega_+)^2(\omega-\omega_+)^2+(-\Gamma\omega^3+\mathrm{Im}\eta_x)^2_{\omega=\omega_+}}\right.$$
$$\left.-\left[\frac{\mathfrak{h}}{\omega}\left(0-(-\Gamma\omega^3-\mathrm{Im}\eta_x)\frac{\partial}{\partial R}\mathrm{Re}\eta_x^*\right)\right]_{\omega=\omega_-}\int_{-\infty}^{\infty}\frac{1}{(2\omega_-)^2(\omega-\omega_-)^2+(-\Gamma\omega^3-\mathrm{Im}\eta_x)^2_{\omega=\omega_-}}\right\}$$
$$=-\pi\left[\left(\frac{\mathfrak{h}^2}{\omega}\frac{\partial}{\partial R}\mathrm{Re}\eta_x^*\right)_{\omega=\omega_+}\left(\frac{\pi}{2\omega_+}\right)-\left(\frac{\mathfrak{h}^2}{\omega}\frac{\partial}{\partial R}\mathrm{Re}\eta_x^*\right)_{\omega=\omega_-}\left(\frac{\pi}{2\omega_-}\right)\right]\Bigg\}. \tag{35}$$

In this case we may not use the lowest approximation for ω_+ and ω_-, but rather must carry the next term in the expansion from (27) and (28),

$$\omega_+ \cong \omega_0 + \tfrac{1}{2}(\mathrm{Re}\eta_x)/\omega_0 \ , \tag{36}$$

$$\omega_- \cong \omega_0 - \tfrac{1}{2}(\mathrm{Re}\eta_x)/\omega_0 \ . \tag{37}$$

Thus

$$F_{2P}^{(x)} = -\left(\frac{\pi^2\mathfrak{h}^2}{2\omega^2}\frac{\partial}{\partial R}\mathrm{Re}\eta_x^*\right)\Bigg|_{\omega=\omega_-}^{\omega=\omega_+}$$
$$\cong -(\omega_+-\omega_-)\frac{\partial}{\partial\omega}\left(\frac{\pi^2\mathfrak{h}^2}{2\omega^2}\frac{\partial}{\partial R}\mathrm{Re}\eta_x\right)_{\omega=\omega_0}$$
$$\cong -\frac{\hbar}{4\omega_0}\mathrm{Re}\eta_x\frac{\partial}{\partial R}\mathrm{Re}\eta_x\frac{\partial}{\partial\omega}\left[\frac{1}{\omega}\coth\left(\frac{\hbar\omega}{2KT}\right)\right]_{\omega=\omega_0} . \tag{38}$$

Adding on the contributions for $F_{2P}^{(y)}$ and $F_{2P}^{(z)}$, we find

$$F_{2P} = -\frac{\hbar}{8\omega_0}\frac{\partial}{\partial R}[(\mathrm{Re}\eta_x)^2+(\mathrm{Re}\eta_y^2)+(\mathrm{Re}\eta_z)^2]$$
$$\times\frac{\partial}{\partial\omega}\left[\frac{1}{\omega}\coth\left(\frac{\hbar\omega}{2KT}\right)\right]_{\omega=\omega_0} , \tag{39}$$

or from (24) and (25),

$$F_{2P} = -\frac{\partial}{\partial R}U_{2P}(R) \ , \tag{40}$$

$$U_{2P}(R) = \frac{3}{4}\frac{\alpha^2\hbar\omega_0^3}{R^6}\frac{\partial}{\partial\omega}\left[\frac{1}{\omega}\coth\left(\frac{\hbar\omega}{2KT}\right)\right]_{\omega=\omega_0} , \tag{41}$$

with α the static polarizability of each oscillator as in (34).

D. Low-temperature limit

At low temperatures $T\to 0$, the potentials obtained in (33) and (41) go over to the familiar unretarded Van der Waals results for absolute zero,

$$\coth(\hbar\omega_0/2KT)\to 1, \quad \text{as } T\to 0 \ , \tag{42}$$

$$U_{PW}(R) = -\alpha\hbar\omega_0/8R^3 \ , \tag{43}$$

$$U_{2P}(R) = -\tfrac{3}{4}\alpha^2\hbar\omega_0/R^6 \ . \tag{44}$$

The first correction at low temperature can be found by writing

$$\coth(\hbar\omega_0/2KT) = (1+\epsilon)/(1-\epsilon)\sim 1+2\epsilon \ , \tag{45}$$

where

$$\epsilon = \exp(-\hbar\omega_0/KT) \ll 1 \ . \tag{46}$$

Thus from (33) and (41), the potentials become

$$U_{PW}(R) \cong -(\alpha\hbar\omega_0/8R^3)[1+2\exp(-\hbar\omega_0/KT)] \ , \tag{47}$$

$$U_{2P}(R) \cong -\frac{3}{4}\frac{\alpha^2\hbar\omega_0}{R^6}\left[1+2\left(1+\frac{\hbar\omega_0}{KT}\right)\exp\left(\frac{-\hbar\omega_0}{KT}\right)\right] . \tag{48}$$

In both cases, the forces are increasing functions of temperature.

E. High-temperature limit

At high temperatures for which

$$\hbar\omega_0/KT \ll 1 \ , \tag{49}$$

we may expand the hyperbolic cotangent as

$$\coth z = 1/z + z/3 - z^3/45 + \tfrac{2}{945}z^5 - \cdots \ , \tag{50}$$

giving

$$U_{PW}(R) \cong -\frac{\alpha\hbar\omega_0}{8R^3}\left(\frac{2KT}{\hbar\omega_0}+\frac{\hbar\omega_0}{6KT}-\cdots\right) \ , \tag{51}$$

and

$$U_{2P}(R) \cong \frac{3}{4}\frac{\alpha^2\hbar\omega_0^3}{R^6}\left[\frac{-4KT}{\hbar\omega_0^3}-\frac{2}{45}\left(\frac{\hbar}{2KT}\right)^3\omega_0+\cdots\right] . \tag{52}$$

Thus in the high-temperature limit, the unretarded potentials are independent of Planck's constant, $\hbar$, and of the natural frequency ω_0 of the oscillator,

$$U_{PW} = -\alpha KT/4R^3 \ , \tag{53}$$

$$U_{2P} = -3\alpha^2KT/R^6 \ . \tag{54}$$

F. High-temperature Van der Waals forces and classical statistical mechanics

In the high-temperature limit the random classical electromagnetic radiation spectrum (5) at fixed frequency ω goes over to the Rayleigh-Jeans law energy of KT per normal mode. The unretarded forces (53) and (54) are just those which are derived from a purely Rayleigh-Jeans radiation spectrum. Now this is also the domain of traditional classical statistical mechanics which ignores the possibility of classical zero-point radiation. Hence it seems of interest to apply traditional classical statistical mechanics to the problem of electric dipole oscillators interacting through an electrostatic dipole interaction and located in a bath at temperature T. The resulting Van der Waals forces are found to be exactly those of Eqs. (53), (54), obtained above from the classical electromagnetic analysis in the high-temperature limit. Thus in this case, the theory of classical electrodynamics with classical electromagnetic zero-point radiation acts to join naturally the familiar quantum results (43), (44) at low temperatures and the traditional classical analysis at high temperatures. As we have noted before, the general results in (33) and (41) obtained from classical theory with zero-point radiation are actually in agreement with the quantum results at every finite temperature. It is generally expected that at high temperatures the quantum results go over to those of traditional classical statistical mechanics.

G. Particle-wall force in classical statistical mechanics

The Van der Waals forces between a polarizable particle and a conducting wall, and between two polarizable particles in contact with a thermal reservoir at temperature T can be obtained from potential functions $\mathcal{U}_{PW}$, $\mathcal{U}_{2P}$ taken from the Helmholtz free energy of the mechanical systems as functions of the separation R,

$$F_{PW}=-\frac{\partial}{\partial R}\mathcal{U}_{PW}(R), \quad F_{2P}=-\frac{\partial}{\partial R}\mathcal{U}_{2P}(R) \ . \tag{55}$$

The Helmholtz free energy can be obtained as an integral over phase space once the Hamiltonian of the mechanical system is given.

In the case of an electric dipole oscillator near a conducting wall, the Hamiltonian[17] is

$$\begin{aligned} H_{PW} &= \frac{\vec{p}^2}{2m}+\tfrac{1}{2}m\omega_0^2\vec{\xi}^2-\frac{e^2}{2}\frac{[\vec{\xi}\cdot\vec{\xi}'-3(\hat{R}\cdot\vec{\xi})(\hat{R}\cdot\vec{\xi}')]}{(2R)^3} \\ &= \frac{\vec{p}^2}{2m}+\tfrac{1}{2}m\omega_0^2\vec{\xi}^2-\frac{e^2}{16R^3}(\xi_x^2+\xi_y^2+2\xi_z^2) \ . \end{aligned} \tag{56}$$

Here R is the distance, chosen along the z axis, of the oscillator from the wall, while $\vec{\xi}$ and $\vec{p}$ are the displacement and momentum, respectively, of the oscillator of charge e, mass m, and frequency ω_0. The displacement $\vec{\xi}'$ of the image dipole is given by

$$\xi_x'=-\xi_x, \quad \xi_y'=-\xi_y, \quad \xi_z'=\xi_z \ . \tag{57}$$

The factor of $\frac{1}{2}$ outside the dipole-energy expression in the first line of (56) arises because the work done in bringing the dipole in from spatial infinity involves forces on the dipole, but not on the image dipole which also moves in from infinity.

The Helmholtz free energy $\mathfrak{F}$ is then

$$\mathfrak{F}=-KT\ln Z \tag{58}$$

with

$$Z=\int_{-\infty}^{\infty} d^3p\,d^3\xi\,\exp(-H_{PW}/KT) \ . \tag{59}$$

The integral for the classical partition function is easily evaluated in the form

$$\int_{-\infty}^{\infty} dx\,\exp(-ax^2)=(\pi/a)^{1/2}, \quad a>0 \ , \tag{60}$$

giving

$$Z=(2\pi mKT)^{3/2}\left(\frac{\pi KT}{\frac{1}{2}m\omega_0^2-e^2/16R^3}\right)^{2/2} \times\left(\frac{\pi KT}{\frac{1}{2}m\omega_0^2-2e^2/16R^3}\right)^{1/2} \ . \tag{61}$$

If we now regard the dipole-dipole interaction as a small perturbation

$$\tfrac{1}{2}m\omega_0^2 \gg e^2/16R^3 \ , \tag{62}$$

we may expand the denominators to obtain

$$Z\cong\left(\frac{2\pi KT}{\omega_0}\right)^3\left(1+\frac{1}{4}\frac{e^2}{m\omega_0^2R^3}\right) \ , \tag{63}$$

and

$$\mathfrak{F}\cong -KT\ln\left(1+\frac{1}{4}\frac{e^2}{m\omega_0^2R^3}\right)-KT\ln\left(\frac{2\pi KT}{\omega_0}\right)^3 \ . \tag{64}$$

Taking the first term in the expansion of the logarithm as

$$\ln(1+x)=x-\tfrac{1}{2}x^2+\tfrac{1}{3}x^3-\cdots \ , \tag{65}$$

and omitting terms which do not depend upon R, we have the potential from the Helmholtz free energy

$$\mathcal{U}_{PW}=-\alpha KT/4R^3 \tag{66}$$

with α the static polarizability of the oscillator as in (34). This is exactly the result obtained above in (53) from classical electromagnetic thermal radiation.

H. Two-particle force in classical statistical mechanics

In the case of two electric dipole oscillators $\vec{\xi}_A$ and $\vec{\xi}_B$ located on the z axis and separated by a distance R, the Hamiltonian is

$$H_{2P} = (1/2m)(\vec{p}_A^2+\vec{p}_B^2) + \tfrac{1}{2}m\omega_0^2(\vec{\xi}_A^2+\vec{\xi}_B^2) + (e^2/R^3)(\xi_{Ax}\xi_{Bx}+\xi_{Ay}\xi_{By}-2\xi_{Az}\xi_{Bz}) \quad . \quad (67)$$

Thus in a thermal bath at temperature T, the classical partition function is given by

$$Z=\int_{-\infty}^{\infty} d^3p_A d^3p_B\, d^3\xi_A d^3\xi_B \exp\left(-\frac{H_{2p}}{KT}\right) \quad . \quad (68)$$

The momentum integrations can be carried out directly using (60). However, it is convenient to change the two variables of integration from $\vec{\xi}_A$ and $\vec{\xi}_B$ over to $\vec{\zeta}_+$ and $\vec{\zeta}_-$ where

$$\vec{\zeta}_+ = (1/\sqrt{2}\,)(\vec{\xi}_A+\vec{\xi}_B) \ , \quad (69)$$

$$\vec{\zeta}_- = (1/\sqrt{2}\,)(\vec{\xi}_A-\vec{\xi}_B) \ .$$

Then the terms in the Hamiltonian depending upon displacement become

$$\tfrac{1}{2}m\omega_0^2(\xi_{Ax}^2+\xi_{Bx}^2)+(e^2/R^3)\xi_{Ax}\xi_{Bx} = \tfrac{1}{2}m\omega_{+x}^2\zeta_{+x}^2+\tfrac{1}{2}m\omega_{-x}^2\,\zeta_{-x}^2 \quad (71)$$

with further equations obtained by replacing the subscript x by y or z and adjusting the coefficient in the term $\xi_{Ax}\xi_{Bx}$. Here the frequencies are

$$\omega_{+x}^2=\omega_{+y}^2=\omega_0^2+e^2/mR^3 \ , \quad (72)$$

$$\omega_{+z}^2=\omega_0^2-2e^2/mR^3 \ , \quad (73)$$

$$\omega_{-x}^2=\omega_{-y}^2=\omega_0^2-e^2/mR^3 \ , \quad (74)$$

$$\omega_{-z}^2=\omega_0^2+2e^2/mR^3 \ . \quad (75)$$

The integrations for the partition function are now easy. The result is

$$Z=(2\pi mKT)^{6/2}\left(\frac{2\pi KT}{m\omega_{+x}^2}\right)^{2/2}\left(\frac{2\pi KT}{m\omega_{-x}^2}\right)^{2/2} \times\left(\frac{2\pi KT}{m\omega_{+z}^2}\right)^{1/2}\left(\frac{2\pi KT}{m\omega_{-z}^2}\right)^{1/2} \quad (76)$$

and

$$\mathfrak{F}=-KT\ln Z = KT(\ln\omega_{+x}^2+\ln\omega_{-x}^2+\tfrac{1}{2}\ln\omega_{+z}^2+\tfrac{1}{2}\ln\omega_{-z}^2) - KT\ln(2\pi KT)^6 \ . \quad (77)$$

We now expand the terms as in (65)

$$\ln\omega_{+x}^2=\ln\left(\omega_0^2+\frac{e^2}{mR^3}\right)=\ln\omega_0^2+\ln\left(1+\frac{e^2}{m\omega_0^2R^3}\right) = \ln\omega_0^2+\frac{e^2}{m\omega_0^2R^3}-\frac{1}{2}\left(\frac{e^2}{m\omega_0^2R^3}\right)^6+\cdots \ , \quad (78)$$

and omit terms independent of the separation R. The interparticle potential from the Helmholtz free energy in (77) becomes

$$\mathfrak{U}_{2P}=-3\left(\frac{e^2}{m\omega_0^2}\right)\frac{KT}{R^6} = -3\,\frac{\alpha^2KT}{R^6} \ , \quad (79)$$

which agrees with the electromagnetic-force result of (54). At high temperatures, the unretarded dispersion forces between electric dipole systems may be obtained from traditional classical statistical mechanics.

IV. ASYMPTOTIC RETARDED VAN DER WAALS FORCES

A. Approximations for large separations

In addition to the simple unretarded forms which we have just considered, the general force expressions (33) and (41) holding at all distances also take simple forms at very large separations R. The requirement of large separation is

$$\omega_0R/c \gg 1 \ , \quad (80)$$

just the opposite limit of Eq. (10). All the initial remarks about the resonant denominators involving C hold true here as in Sec. III. However, the sine and cosine terms $\exp(i2kR)$ and $\exp(ikR)$ appearing in Eqs. (17)–(20) for Σ and η are rapidly varying through the resonance because of the large distance condition (80). Thus the resonant contributions to the integrals are washed out, and it is only the low-frequency parts which give significant contributions to the integrals (33) and (41).

In the low-frequency range, we may approximate C from Eq. (15) as

$$C=-\omega^2+\omega_0^2-i\Gamma\omega^3\cong\omega_0^2 \ . \quad (81)$$

Also, when R is large and the frequency ω is small, the terms Σ and η are small. Hence we may write the logarithmic terms in (33) and (41) as

$$\ln\left(1+\frac{\Sigma_x}{C}\right)\cong\frac{\Sigma_x}{\omega_0^2}, \quad \ln\left(1-\frac{\eta_x^2}{C^2}\right)\cong-\frac{\eta_x^2}{\omega_0^4}, \quad (82)$$

and so obtain for the large R asymptotic forms

$$U_{PW}(R) = \frac{\hbar}{2\pi}\int_{\omega=0}^{\infty}\frac{d\omega}{\omega_0^2}\coth\left(\frac{\hbar\omega}{2KT}\right)\times[\mathrm{Im}(\Sigma_x+\Sigma_y+\Sigma_z)], \quad (83)$$

$$U_{2P}(R) = \frac{\hbar}{2\pi}\int_{\omega=0}^{\infty}\frac{d\omega}{\omega_0^4}\coth\left(\frac{\hbar\omega}{2KT}\right)\times[\mathrm{Im}(-\eta_x^2-\eta_y^2-\eta_z^2)]. \quad (84)$$

B. Asymptotic forms at finite temperature

Substituting the explicit forms of Σ and η, we have

$$U_{PW}(R) = \frac{\hbar c\alpha}{2\pi}\int_{k=0}^{\infty}dk\coth\left(\frac{\hbar ck}{2KT}\right)\times\left(\frac{k^2}{R}\sin 2kR+\frac{k}{R^2}\cos 2kR-\frac{1}{2R^3}\sin 2kR\right), \quad (85)$$

$$U_{2P}(R) = -\frac{\hbar c\alpha^2}{\pi}\int_{k=0}^{\infty}dk\,k^6\coth\left(\frac{\hbar ck}{2KT}\right)\times\left(\frac{\sin 2kR}{(kR)^2}+\frac{2\cos 2kR}{(kR)^3}-\frac{5\sin 2kR}{(kR)^4}-\frac{6\cos 2kR}{(kR)^5}+\frac{3\sin 2kR}{(kR)^6}\right). \quad (86)$$

At low temperature $T\to 0$, $\coth(\hbar ck/2KT)\to 1$, and we recognize familiar equations for the asymptotic retarded dispersion forces; the first equation (85) is given explicitly by Casimir,[18] and the second is written out elsewhere.[19] The zero-temperature results are

$$U_{PW}(R) = -(3/8\pi)(\alpha\hbar c/R^4) \quad (87)$$

and

$$U_{2P}(R) = -(23/4\pi)(\alpha^2\hbar c/R^7). \quad (88)$$

The potentials at finite temperature may be obtained by use of the integral[20]

$$\int_{k=0}^{\infty}dk\sin ak\,(\coth\beta k-1) = (\pi/2\beta)\coth(a\pi/2\beta)-1/a, \quad \mathrm{Re}\beta>0. \quad (89)$$

All the integrals are evaluated with the temporary use of a smooth cutoff at high frequencies. Thus for example the integral $\int_0^\infty dk\sin ak$ is obtained as

$$\int_{k=0}^{\infty}dk\sin(ak)\exp(-\lambda k) = \mathrm{Im}\int_{k=0}^{\infty}dk\exp[(-\lambda+ia)k] = -\mathrm{Im}(-\lambda+ia)^{-1}\to a^{-1} \quad \text{as } \lambda\to 0. \quad (90)$$

Thus from (89) above we write

$$\int_{k=0}^{\infty}dk\sin ak\coth\beta k = (\pi/2\beta)\coth(a\pi/2\beta), \quad (91)$$

$$\int_{k=0}^{\infty}dk\,k\cos ak\coth\beta k = \frac{\partial}{\partial a}\int_{k=0}^{\infty}dk\sin ak\coth\beta k, \quad (92)$$

with similar expressions for higher powers of k.

Using these integrals for the evaluation of (85) and (86), we find for finite temperatures,

$$U_{PW}(R) = \alpha KT\left(-\frac{1}{8R}\frac{\partial^2}{\partial R^2}+\frac{1}{4R^2}\frac{\partial}{\partial R}-\frac{1}{4R^3}\right)\times\coth\left(\frac{2\pi KTR}{\hbar c}\right) \quad (93)$$

and

$$U_{2P}(R) = \alpha^2 KT\left(-\frac{1}{16R^2}\frac{\partial^4}{\partial R^4}+\frac{1}{4R^3}\frac{\partial^3}{\partial R^3}-\frac{5}{4R^4}\frac{\partial^2}{\partial R^2}+\frac{3}{R^5}\frac{\partial}{\partial R}-\frac{3}{R^6}\right)\coth\left(\frac{2\pi KTR}{\hbar c}\right). \quad (94)$$

In the limit of low temperatures, we can expand the hyperbolic cotangent as in (50) and so recover the zero-temperature expressions (87), (88). In the limit of high temperatures or large distances

$$2\pi KTR/\hbar c\gg 1, \quad (95)$$

the hyperbolic cotangent approaches the value 1, so (93) and (94) become

$$U_{PW}(R) = -\alpha KT/4R^3, \quad (96)$$

$$U_{2P}(R) = -3\alpha^2 KT/R^6. \quad (97)$$

The results here (96) and (97) for the high-temperature limits at large distances are identical with the unretarded results in (53) and (54) holding in the high-temperature limit at short distances.

C. Failure of Casimir-Polder R^{-7} asymptotic form at finite temperature

We note that for any nonzero finite temperature, the separation R can be chosen sufficiently large such that the condition (95) is satisfied. Hence asymptotically the two-particle potential goes to the form R^{-6}. Thus we find a curious situation. At short distances

$$\omega_0 R/c\ll 1 \quad (98)$$

compared to the natural frequency of the oscillator, the unretarded Van der Waals potential (41) is of the form R^{-6} for all temperatures. Next, if the temperature is sufficiently low that there is a region of separations such that

$$c/\omega_0\ll R\ll\hbar c/2\pi KT, \quad (99)$$

then the potential goes over to the Casimir-Polder[21] form R^{-7}. This corresponds to a separation between the particles long compared to the wavelength radiated at the natural frequency of the oscillator, but sufficiently short that the random radiation spectrum is still dominated by zero-point radiation and not the thermal radiation. However, at sufficiently low frequencies, the thermal radiation takes the Rayleigh-Jeans form KT per normal mode which dominates the zero-point form, $\frac{1}{2}\hbar\omega$. Thus asymptotically for large R and any finite temperature, the potential falls off as R^{-6}. If the temperature is sufficiently high, there may be no separation R satisfying the condition (99), and hence no separation obeying the Casimir-Polder asymptotic form.

D. Classical statistical mechanics and asymptotic retarded forces

In the case of the unretarded Van der Waals forces, we emphasized that for high temperatures the forces may be derived from traditional classical statistical mechanics. The analogous result holds for the asymptotic retarded forces.

In the Coulomb gauge the Hamiltonian for electric dipole oscillator systems may be written as

$$H=\sum_\alpha\left[\frac{1}{2m_\alpha}\left(\vec{p}_\alpha-\frac{e_\alpha}{c}\vec{A}(\vec{r}_\alpha,t)\right)^2+\tfrac{1}{2}m\omega_0^2\vec{\xi}_\alpha^{\,2}\right]+\frac{1}{8\pi}\int|\nabla\Phi|\,d^3r+\frac{1}{8\pi}\int d^3r\,(\vec{E}_\perp^2+\vec{B}^2). \qquad (100)$$

The dipole approximation is introduced in evaluating the vector potential $\vec{A}$ at the average position $\vec{r}_\alpha$ of the oscillator rather than including the displacement $\vec{\xi}_\alpha$. In the case of the unretarded Van der Waals forces, only the first three terms for H in (100) were included in the calculation of the partition function Z. These included the oscillator kinetic energy $\frac{1}{2}m\dot{\vec{\xi}}_\alpha^{\,2}$, the mechanical potential energy $\frac{1}{2}m\omega_0^2\vec{\xi}_\alpha^{\,2}$, and the Coulomb electrostatic interaction. The change with R of terms involving the transverse fields was regarded as negligible. The situation is just reversed for the asymptotic retarded forces. Now the dependence upon the separation R is contained in the transverse field energy $(1/8\pi)\int(\vec{E}_\perp^2+\vec{B}^2)\,d^3r$ for the low frequencies.

At low frequencies we may neglect the terms involving $d^2\vec{\xi}/dt^2$ and $d^3\vec{\xi}/dt^3$ in the oscillator equation of motion. The displacement is in phase with the driving electric field

$$\vec{\xi}=(e/m\omega_0^2)\vec{E}(\vec{r},t). \qquad (101)$$

The oscillator then radiates energy due to its electric dipole moment

$$e\vec{\xi}=\alpha\vec{E}(\vec{r},t), \qquad (102)$$

with the static polarizability as in (34). Hence the transverse fields $\vec{E}_\perp$ and $\vec{B}$ must include not only the contributions $\vec{E}_0$ and $\vec{B}_0$ present in the absence of the oscillator but also the field due to the oscillator. The last term in (100) thus depends upon the separation R through the behavior of the transverse electric fields.

The transverse field part of the Hamiltonian (100) can be rewritten in the form[22]

$$H_{\rm EM}=\sum_\lambda\tfrac{1}{2}(p_\lambda^2+\omega_\lambda^2q_\lambda^2), \qquad (103)$$

where the transverse fields have been expanded in normal modes of the volume V as

$$\vec{E}=\left(\frac{4\pi}{V}\right)^{1/2}\sum_\lambda p_\lambda(t)\vec{f}_\lambda(\vec{r}), \qquad (104)$$

$$\vec{B}=-c\left(\frac{4\pi}{V}\right)^{1/2}\sum_\lambda q_\lambda(t)\nabla\times\vec{f}_\lambda(\vec{r}) \qquad (105)$$

with the $\vec{f}_\lambda(\vec{r})$ as orthonormal functions satisfying

$$(-\nabla\times\nabla+k_\lambda^2)\vec{f}_\lambda(\vec{r})=0\,,\quad \nabla\cdot\vec{f}_\lambda(\vec{r})=0\,. \qquad (106)$$

Hence the partition function is

$$Z=\int\prod_\lambda dp_\lambda\,dq_\lambda\exp\left(-\frac{\sum_\lambda\frac{1}{2}(p_\lambda^2+\omega_\lambda^2q_\lambda^2)}{KT}\right)=\prod_\lambda(2\pi KT)^{1/2}\left(\frac{2\pi KT}{\omega_\lambda^2}\right)^{1/2}=\prod_\lambda\frac{2\pi KT}{\omega_\lambda}, \qquad (107)$$

and the Helmholtz free energy

$$\mathfrak{F}=-KT\ln Z=-KT\sum_\lambda\ln(2\pi KT/\omega_\lambda)=KT\sum_\lambda\ln\omega_\lambda-KT\sum_\lambda\ln(2\pi KT). \qquad (108)$$

Now Casimir[23] has shown that the presence of electrically polarizable particles leads to shifts $\delta\omega_\lambda$ in the resonant frequencies ω_λ of the cavity in the form

$$\frac{\delta\omega_\lambda}{\omega_{\lambda0}}\cong\frac{-\frac{1}{2}\alpha E_0^2}{(1/8\pi)\int d^3r\,(\vec{E}_{\lambda0}^2+\vec{B}_{\lambda0}^2)}, \qquad (109)$$

where $\omega_{\lambda0}$, $\vec{E}_0$, and $\vec{B}_0$ were the resonant frequencies and fields before the introduction of the polarizable particle with polarizability α. Hence we have the Helmholtz free energy given by

$$\mathfrak{F}=KT\sum_\lambda\ln(\omega_{\lambda0}+\delta\omega_\lambda)-KT\sum_\lambda\ln(2\pi KT)=KT\sum_\lambda\ln(1+\delta\omega_\lambda/\omega_{\lambda0})-KT\sum_\lambda\ln(2\pi KT/\omega_{\lambda0}). \qquad (110)$$

Expanding the logarithm as in (65), and noting that the last term is independent of the changes in frequency due to the polarizable particle, we have a potential function associated with changes in Helmholtz free energy

$$\mathcal{U} = KT \sum_{\lambda} \frac{\delta\omega_\lambda}{\omega_{\lambda 0}}. \tag{111}$$

Furthermore, the denominator in (109) involves the energy of the normal mode λ before the introduction of the last polarizable particle, and hence at thermal equilibrium in traditional classical statistical mechanics

$$(1/8\pi)\int d^3r\,(\vec{E}^2_{\lambda 0} + \vec{B}^2_{\lambda 0}) = KT. \tag{112}$$

This leaves

$$\delta\omega_\lambda/\omega_{\lambda 0} = -\tfrac{1}{2}\alpha \vec{E}^2_{\lambda 0}/KT$$

and

$$\mathcal{U} = -\tfrac{1}{2}\alpha \sum_{\lambda} \vec{E}^2_{\lambda 0} = \tfrac{1}{2}\alpha\langle \vec{E}^2_0\rangle \tag{113}$$

where the angular brackets refer to a time average over the unperturbed electric field.

However, the result (113) is exactly the starting place of Eq. (10) in Ref. 8 for the analysis of asymptotic retarded Van der Waals forces in classical electrodynamics with classical electromagnetic zero-point radiation. We merely replace the spectral function for the random radiation by the Rayleigh-Jeans form KT per normal mode, we are led to equations of the form (17) and (29) of Ref. 8 which correspond to the high-temperature limits given above in (96) and (97) following from (93) and (94). Thus traditional classical statistical mechanics gives the same result for the high-temperature limit as is obtained in our previous electromagnetic-force calculations.

V. FORCES BETWEEN CONDUCTING PARALLEL PLATES

A. Connections with the asymptotic retarded force calculations

In 1948 Casimir[6] predicted that two unchanged conducting parallel plates would have a Van der Waals force between them given by a potential

$$\mathcal{U}(d) = (-\pi^2/720)(\hbar c L^2/d^3) \tag{114}$$

where L^2 is the surface area of each of the plates and d is the separation between them. The temperature dependence of this force has been investigated[5] a number of times and the recent calculations are believed to be accurate so that no full calculation is needed on our part. However, the ideas involved in the parallel plate calculations fit so neatly with the asymptotic retarded Van der Waals forces discussed above that we will include some remarks on this situation.

The electromagnetic interaction of two conducting parallel plates is described in terms of the normal modes of the electromagnetic radiation field between the plates. The conducting boundary conditions serve to define the normal modes, but the energy and entropy are assigned exclusively to the electromagnetic field. This is exactly the situation which we found held asymptotically at large separations for the retarded Van der Waals forces. At temperature $T=0$, one may consider the zero-point radiation between the plates $\frac{1}{2}\hbar\omega$ per normal mode and so obtain Casimir's potential (114) above. However, at finite temperature, one must consider the Helmholtz free energy of the radiation.

Now in our previous calculations in this paper, we have approached the Van der Waals forces from two directions. In our first calculations, we took a given spectrum of random radiation and then obtained the forces by strictly electromagnetic theory. In our second point of view, we looked at the forces in terms of statistical mechanics. Most of the previous finite-temperature calculations for conducting plates pursue the statistical mechanical approach from a quantum point of view. Hence following through on our parallel treatment, we note that one can also carry through a purely classical electromagnetic-force calculation.

The forces between two conducting plates immersed in random classical electromagnetic radiation can be obtained by evaluating the Maxwell stress tensor over one of the plates. The analysis has been carried out at zero temperature in Ref. 11, and can be carried out at finite temperature merely by inserting the random-radiation spectrum (5) in Eqs. (20) and (25) of Ref. 11. Thus equation (25) there for plates of area $A=L^2$ becomes

$$\begin{aligned}\int dy \int dz\,\langle T_{xx}(d_-,y,z,t)\rangle &= \sum_{n=0} \int_0^\infty dk_y \int_0^\infty dk_z \frac{L^2\hbar c}{\pi^2}\left(\coth\frac{\hbar\omega}{2KT}\right)\frac{k_x^2}{kd}\\ &= -\frac{\partial}{\partial d}\sum_{n_x=0}^{\infty}\int_0^\infty dn_y \int_0^\infty dn_z \left\{\tfrac{1}{2}\hbar\omega + KT\ln\left[1-\exp\left(-\frac{\hbar\omega}{KT}\right)\right]\right\},\end{aligned} \tag{115}$$

where here for two conducting parallel plates the frequencies of the normal modes are

$$\omega = c\left[\left(\frac{n_x\pi}{d}\right)^2 + \left(\frac{n_y\pi}{L}\right)^2 + \left(\frac{n_z\pi}{L}\right)^2\right]^{1/2}. \tag{116}$$

The expression $\frac{1}{2}\hbar\omega + KT\ln[1-\exp(-\hbar\omega/KT)]$ is just the Helmholtz free energy of the radiation mode of the frequency ω. Thus the Maxwell stress tensor leads to an expression which is just the derivative of a potential function which is the Helmholtz free energy of the electromagnetic field. The full calculations for the Van der Waals forces have been carried out by Sauer and by Mehra in Ref. 5.

B. Limiting forms of the parallel-plate force

At low temperatures the zero-point radiation gives the dominant force between conducting parallel plates, and one obtains Casimir's potential (114) depending on the separation as d^{-3}. However, in exact analogy with the results of Sec. IV for the asymptotic retarded forces, one finds that at high temperatures or large separations d between the plates, the thermal radiation spectrum gives the dominant contribution and the force law changes to d^{-2} for the potential.

Qualitatively the situation is easy to understand. Just as in Sec. IV, one finds that the frequencies ω which contribute significantly to the force between the plates are those for which

$$\omega d/c \sim 1 . \tag{117}$$

The effects of higher frequency modes tend to cancel out. Thus the force is dominated by the character of the random radiation spectrum at frequencies satisfying (117). In thermal equilibrium, the character of the spectrum is indicated by a comparison between the zero-point radiation $\frac{1}{2}\hbar\omega$ per normal mode and the high-temperature limit KT per normal mode. Thus when the temperature is low or the separation between the plates is small

$$KT \ll \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar c/d , \tag{118}$$

so that the zero-point radiation dominates and Eq. (114) holds. On the other hand, for high temperatures or large separations

$$KT \gg \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar c/d , \tag{119}$$

so that the Rayleigh-Jeans spectrum dominates and the distance dependence of the force is changed to d^{-2} from Casimir's d^{-3}.

C. Force between conducting plates due to the Rayleigh-Jeans spectrum

In our work on oscillators above in Sec. IV, we found that the asymptotic retarded Van der Waals forces at finite temperature could be derived from electromagnetic forces due to a Rayleigh-Jeans random radiation spectrum, or indeed from traditional classical statistical mechanics. The same is true for the force between conducting parallel plates at large separations or high temperatures. Apparently this is unexpected to some of those who have calculated the finite temperature corrections to the zero-point force between conducting parallel plates. Brown and Maclay[24] obtain this force term which they notice is independent of $\hbar$ and hence term "classical," but they refer to its "physical significance" as "unclear." The force between the conducting plates arises from the discreteness of the normal modes enforced by the conducting boundary conditions. There is nothing quantum mechanical about the force. The particular form of the force depends upon the spectrum of random radiation present. The $U \propto d^{-3}$ force law at low temperature follows from the zero-point spectrum $\frac{1}{2}\hbar\omega$ per normal mode, and the $U \propto d^{-2}$ force law at high temperatures follows from the Rayleigh-Jeans spectrum KT per normal mode.

In order to reinforce the reader's appreciation of the fact that the Rayleigh-Jeans radiation spectrum indeed causes a force between conducting parallel plates, we will carry out the calculation explicitly. At no place does Planck's constant $\hbar$ enter the calculation. The random radiation is exactly as in Eq. (1) with the spectrum now given by the Rayleigh-Jeans form

$$\pi^2 \mathfrak{h}^2 = KT . \tag{120}$$

We consider two conducting plates of area L^2, one located at $x=0$ and the other at $x=d$. Proceeding exactly as in Ref. 11 with this new spectrum, the evaluation of the Maxwell stress tensor leads to

$$F_-(d) = \int dy \int dz \,\langle T_{xx}(d_-, y, z, t)\rangle$$

$$= \sum_{n_x=1}^{\infty} \int_0^\infty dk_y \int_0^\infty dk_z \frac{2L^2KT}{\pi^2}\frac{k_x^2}{k^2 d} , \tag{121}$$

with

$$k_x = n_x\pi/d , \quad \omega = c(k_x^2 + k_y^2 + k_z^2)^{1/2} , \tag{122}$$

as the force on the plate at $x=d$ due to the electromagnetic radiation in the region between the plates. There is also a force on the plate due to the radiation on the far side of the plate at $x=d$. This region is unbounded and so involves only integrals over continuous modes

$$F_+ = \int dy \int dz \,\langle T_{xx}(d_+, y, z, t)\rangle$$

$$= -\int_0^\infty dk_x \int_0^\infty dk_y \int_0^\infty dk_z \frac{2L^2KT}{\pi^3}\frac{k_x^2}{k^2} . \tag{123}$$

The form F_+ follows that of (121) except for the direction of the force and the fact that the sum over n_x is replaced by an integral dn_x with

$$dn_x \pi/d \to dk_x . \tag{124}$$

The total force on the conducting wall is given by

$$F = F_-(d) + F_+ . \tag{125}$$

Now the two expressions $F_-(d)$ and F_+ both involve divergent integrals. However, this divergence is unphysical. Actually the plates will be good conductors at low frequencies but will cease to be conducting at high frequencies. Hence we introduce in each integrand a cutoff at high frequencies $\exp(-\lambda\omega/\pi c)$ where λ corresponds roughly to the wavelength where the wall becomes transparent to radiation. We will find that we can take $\lambda\to 0$ at the end of the calculation; in other words, the forces on the plates are independent of any cutoff provided the plates are good conductors. Inserting the cutoff function, the expressions of (121) and (123) become absolutely convergent integrals

$$F_-(d,\lambda)=\sum_{n_x=1}^{\infty}\int_0^\infty dk_y\int_0^\infty dk_z\frac{2L^2KT}{\pi^2}\frac{k_x^2}{k^2d}\exp\left(-\frac{\lambda\omega}{\pi c}\right), \tag{126}$$

$$F_+(\lambda)=-\int_0^\infty dk_x\int_0^\infty dk_y\int_0^\infty dk_z\frac{2L^2KT}{\pi^3}\frac{k_x^2}{k^2}\exp\left(-\frac{\lambda\omega}{\pi c}\right). \tag{127}$$

The integral for $F_+(\lambda)$ may be evaluated easily in spherical polar coordinates yielding

$$F_+(\lambda)=-\frac{2\pi}{3}\frac{L^2KT}{\lambda^3}. \tag{128}$$

The expression for $F_-(d,\lambda)$ requires more attention. We introduce polar coordinates r, ϕ

$$k_x=\pi r\cos\phi,\quad k_y=\pi r\sin\phi\,, \tag{129}$$

and we denote n_x by n. Then integrating over ϕ, Eq. (126) becomes

$$F_-(d,\lambda)=\frac{2\pi}{4}\frac{2L^2KT}{d}\sum_{n=1}^{\infty}\int_{r=0}^\infty dr\,r\,\frac{(n/d)^2}{(n^2/d^2+r^2)}\times\exp[-\lambda(n^2/d^2+r^2)^{1/2}]. \tag{130}$$

Next we change the variable of integration from r over to

$$z=(d^2/n^2)r, \tag{131}$$

so that

$$\begin{aligned}F_-(d,\lambda)&=\frac{\pi L^2KT}{2d}\sum_{n=1}^{\infty}\int_{z=0}^\infty\frac{dz}{1+z}\frac{n^2}{d^2}\exp\left(-\frac{\lambda n(1+z)^{1/2}}{d}\right),\\&=\frac{\pi L^2KT}{2d}\frac{\partial^2}{\partial\lambda^2}\int_{z=0}^\infty\frac{dz}{(1+z)^2}\sum_{n=1}^{\infty}\exp\left(-\frac{n\lambda(1+z)^{1/2}}{d}\right).\end{aligned} \tag{132}$$

The sum over n now involves a geometric series

$$\sum_{n=1}^{\infty}\exp\left(-\frac{n\lambda(1+z)^{1/2}}{d}\right)=\frac{\exp[-\lambda(1+z)^{1/2}/d]}{1-\exp[-\lambda(1+z)^{1/2}/d]}=\frac{1}{\exp[\lambda(1+z)^{1/2}/d]-1}. \tag{133}$$

At this point we change the variable of integration yet again to

$$u=\lambda(1+z)^{1/2}/d, \tag{134}$$

giving

$$F_-(d,\lambda)=\frac{\pi L^2KT}{d}\frac{\partial^2}{\partial\lambda^2}\frac{\lambda^2}{d^2}\int_{u=\lambda/d}^\infty\frac{du}{u^3}\frac{1}{e^u-1}. \tag{135}$$

It is possible to complete the evaluation of $F_-(d,\lambda)$ by breaking the integral into two parts

$$\int_{u=\lambda/d}^\infty\frac{du}{u^3}\frac{1}{e^u-1}=\int_{u=\lambda/d}^{u=1}\frac{du}{u^3}\frac{1}{e^u-1}+\int_{u=1}^\infty\frac{du}{u^3}\frac{1}{e^u-1}, \tag{136}$$

calculating the second integral numerically on a computer, while expanding the integrand[25] in the first term as a power series in u, converging for $|u|<2\pi$, which can then be integrated term by term. However, a more elegant mathematical prescription is given below.

The integrand in (136) can be expanded as

$$\frac{1}{e^u-1}=\frac{e^{-u/2}}{e^{u/2}-e^{-u/2}}=\tfrac{1}{2}(\coth\tfrac{1}{2}u-1) \tag{137}$$

with[26]

$$\coth\tfrac{1}{2}u=\frac{2}{u}+u\sum_{n=1}^{\infty}\frac{1}{n^2\pi^2+\frac{1}{4}u^2} \tag{138}$$

so that

$$\frac{1}{e^u-1}=\frac{1}{2}\left(-1+\frac{2}{u}+u\sum_{n=1}^{\infty}\frac{1}{n^2\pi^2+\frac{1}{4}u^2}\right). \tag{139}$$

We now use this expression in the integral of (136), integrating term by term and employing partial fractions for the integrands $2/[u^2(u^2+4n^2\pi^2)]$,

$$\int_{u=x}^\infty\frac{du}{u^3}\frac{1}{e^u-1}=-\frac{1}{4x^2}+\frac{1}{3x^3}+\sum_{n=1}^{\infty}\frac{1}{2n^2\pi^2}\left[\frac{1}{x}-\left(\frac{\pi}{2}-\tan^{-1}\frac{x}{2n\pi}\right)\frac{1}{2n\pi}\right]. \tag{140}$$

However, we may introduce the Riemann zeta function[27]

$$\zeta(z)=\sum_{n=1}^{\infty}\frac{1}{n^z},\quad \mathrm{Re}\,z>1, \tag{141}$$

so that (140) becomes

$$\int_{u=x}^\infty\frac{du}{u^3}\frac{1}{e^u-1}=-\frac{1}{4x^2}+\frac{1}{3x^3}+\frac{\zeta(2)}{2\pi^2x}-\frac{\zeta(3)}{8\pi^2}+\sum_{n=1}^{\infty}\frac{1}{4n^3\pi^3}\tan^{-1}\frac{x}{2n\pi}. \tag{142}$$

The arctangent function can be expanded[28] as a power series in x

$$\tan^{-1}\frac{x}{2n\pi}=\sum_{p=0}^{\infty}\frac{(-1)^p}{2p+1}\left(\frac{x}{2n\pi}\right)^{2p+1}. \tag{143}$$

Introducing this expansion into the last term of (142), interchanging the orders of summation so as to obtain zeta functions as in (141), and noting[29]

$$\zeta(2p+4)=\frac{(-1)^{p+1}(2\pi)^{2p+4}}{2(2p+4)!}\,B_{2p+4}\,, \tag{144}$$

we have

$$\int_{u=x}^{\infty}\frac{du}{u^3}\,\frac{1}{e^u-1}=-\frac{1}{4x^2}+\frac{1}{3x^3}+\frac{\zeta(2)}{2\pi^2 x}-\frac{\zeta(3)}{8\pi^2}-\sum_{p=0}^{\infty}\frac{x^{2p+1}B_{2p+4}}{(2p+4)!(2p+1)}\,. \tag{145}$$

This series expansion can be inserted in Eq. (135), giving

$$F_-(d,\lambda)=\pi L^2KT\left(\frac{2}{3\lambda^3}-\frac{\zeta(3)}{4\pi^2d^3}+\frac{\lambda}{120d^4}+\cdots\right)\,. \tag{146}$$

Combining (146) for $F_-(d,\lambda)$ and (128) for $F_+(\lambda)$, we see that the term in λ^{-3} cancels, and the remaining terms are independent of the cutoff λ or else of the order λ^n/d^{n+3}. In the limit of good conductors compared to the separation, $\lambda/d\ll 1$, we may take $\lambda=0$. This gives the result which also holds for a perfect conductor. Thus the force between two conducting parallel plates emersed in thermal radiation with a Rayleigh-Jeans spectrum is

$$F(d)=-\frac{\zeta(3)L^2KT}{4\pi d^3} \tag{147}$$

or

$$F(d)=-\frac{\partial u}{\partial d},\ U(d)=-\frac{\zeta(3)}{8\pi}\,\frac{L^2KT}{d^2}\,. \tag{148}$$

This agrees with Mehra's result[5] for the high-temperature limit of the force based on Planck's radiation spectrum.

VI. CLOSING SUMMARY

The Van der Waals forces between polarizable objects which have no permanent dipole moments are generally classed as dispersion forces. London[30] in 1930 first showed that such forces appeared from quantum considerations involving the electrostatic interaction of electric dipole systems at the absolute zero of temperature. In 1948 Casimir and Polder[21] extended the understanding of these forces by including the interaction of the quantum electromagnetic field at absolute zero.

Also in 1948 Casimir[6,18] introduced a new method of calculating Van der Waals forces based upon essentially classical electromagnetic boundary conditions together with the assignment of an energy spectrum $\frac{1}{2}\hbar\omega$ per normal mode to the electromagnetic field. This point of view has been broadened[8-16] to form a classical electromagnetic theory in which the homogeneous boundary condition on Maxwell's equations is specified by random zero-point radiation with a Lorentz invariant spectrum. The undetermined constant for the spectrum is chosen to give agreement with the familiar $\frac{1}{2}\hbar\omega$.

In this classical theory, dispersion forces are easily understood. The random electromagnetic field sets material systems into random motion and the classical electromagnetic interactions among the systems lead to Van der Waals forces. These forces have been computed[8-11] for electric dipole oscillator systems and are in exact agreement with quantum results. However, classical thermal radiation at finite temperature is qualitatively the same as at zero temperature; only the spectrum is changed. Hence all the previous calculations can be repeated for the new spectrum of random radiation. This is what we have done in this paper. In contrast with quantum perturbation theory which requires a new analysis involving sums over excited states, we have merely inserted the new spectrum into our previous classical calculation. We then saw how the general expression for the force at all separations simplified at small separations giving unretarded expressions and at large separations giving asymptotic retarded forms. Moreover, we have shown how at high temperatures the results agree with the use of the Rayleigh-Jeans spectrum for the random radiation and also with the application of traditional classical statistical mechanics which has no role for zero-point fluctuations.

The presence of the thermal radiation in addition to the zero-point radiation increases the strength of the Van der Waals forces. The specific constant obtained in (41) for the unretarded R^{-6} attraction at short distances depends upon the assumed harmonic oscillator structure of the material systems. However, at large distances, the low-frequency electromagnetic field fluctuations play the dominant role irrespective of the details of the material system; the asymptotic retarded force (94) depends only upon the static polarizability of the matter. One of the curious results of our calculations is the observation that at any finite temperature, the thermal-radiation spectrum eventually dominates the Van der Waals force behavior for large enough separations. Thus for $T>0$, the long-range asymptotic form for the force between two polarizable particles will eventually change from the Casimir-Polder R^{-7} potential dependent upon Planck's constant $\hbar$ over to an R^{-6} potential dependent upon KT.

The new results on the Van der Waals forces between polarizable particles are in agreement with the earlier calculations of other researchers[5-7] on the forces between conducting parallel plates. At small separations where the high-frequency spectrum of random radiation determines the force, the zero-point radiation predominates giving Casimir's d^{-3} potential depending upon Planck's constant $\hbar$. At large separations where the low-frequency spectrum of random radiation determines the force, we have $KT > \frac{1}{2}\hbar\omega$ and the Rayleigh-Jeans spectrum produces a d^{-2} potential depending upon KT.

ACKNOWLEDGMENT

I wish to thank Dr. J. Gersten, Dr. G. Feinberg, Dr. M. Mittleman, Dr. L. J. Swank and Dr. M. J. Swank for helpful comments.

---

*Work supported in part by a grant from the City University of New York Faculty Research Award Program.

[1]A recent review of some aspects of Van der Waals forces is given by D. Langbein, *Advances in Solid State Physics, Festkörperprobleme* (Academic, New York, 1973), Vol. 13, p. 85.

[2]Recent theoretical publications include work by G. Feinberg and J. Sucher, J. Chem. Phys. 48, 3333 (1968); Phys. Rev. A 2, 2395 (1970); M. J. Renne, Physica 53, 193 (1971); T. H. Boyer, Phys. Rev. 180, 19 (1969); Phys. Rev. A 5, 1799 (1972); 6, 314 (1972); 7, 1832 (1973); 9, 2078 (1974). See also the papers mentioned in Ref. 1.

[3]Reports of recent experimental work include those by D. Tabor and R. H. S. Winterton, Nature (Lond.) 219, 1120 (1968); Proc. R. Soc. Lond. A 312, 435 (1969); R. H. S. Winterton, Contemp. Phys. 11, 559 (1970); J. N. Israelachvili and D. Tabor, Proc. R. Soc. Lond. A 331, 19 (1972); A. Shih, D. Raskin, and P. Kusch, Phys. Rev. A 9, 652 (1974); A. Shih, Phys. Rev. A 9, 1507 (1974).

[4]See the references listed in Ref. 1.

[5]M. Fierz, Helv. Phys. Acta 33, 855 (1960). (Note that Fierz's calculations are in error because he fails to use the Helmholtz free energy.) F. Sauer, thesis (Gottingen, 1962) (unpublished). C. M. Hargreaves, Proc. K. Ned. Akad. Wet. B 68, 231 (1965); J. Mehra, Physica 37, 145 (1967); T. H. Boyer, Phys. Rev. 174, 1631 (1968); L. S. Brown and G. J. Maclay, Phys. Rev. 184, 1272 (1969).

[6]H. B. G. Casimir, Proc. K. Ned. Akad. Wet. B 51, 793 (1948).

[7]E. M. Lifshitz, Zh. Eksp. Teor. Fiz. 29, 94 (1955) [Sov. Phys.—JETP 2, 73 (1956)]; L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley, New York, 1960), Chap. 13; I. E. Dzyaloschinskii, E. M. Lifshitz, and L. P. Pitaevskii, Adv. Phys. 10, 165 (1961).

[8]T. H. Boyer, Phys. Rev. A 5, 1799 (1972).

[9]T. H. Boyer, Phys. Rev. A 6, 314 (1972).

[10]T. H. Boyer, Phys. Rev. A 7, 1832 (1973).

[11]T. H. Boyer, Phys. Rev. A 9, 2078 (1974).

[12]M. J. Renne, Physica 53, 193 (1971).

[13]T. H. Boyer, Phys. Rev. D 11, 790 (1975); 809 (1975).

[14]T. W. Marshall, Proc. R. Soc. Lond. A 276, 475 (1963).

[15]T. H. Boyer, Phys. Rev. 182, 1374 (1969).

[16]T. W. Marshall, Proc. Camb. Philos. Soc. 61, 537 (1965); Nuovo Cimento 38, 206 (1965); L. L. Henry and T. W. Marshall, *ibid.* 41, 188 (1966); T. H. Boyer, Phys. Rev. 186, 1304 (1969); Phys. Rev. D 1, 1526 (1970); 1, 2257 (1970). See also Refs. 8–15.

[17]See J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), p. 102. See also Ref. 9, Eq. (30).

[18]H. B. G. Casimir, J. Chim. Phys. 46, 407 (1949). See the bottom of p. 408; there is a misprinted overall minus sign.

[19]T. H. Boyer, Phys. Rev. 180, 19 (1969). See Eq. (24).

[20]I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1965), fourth ed., p. 507, Eq. (3.987 No. 2).

[21]H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).

[22]See, for example, E. A. Power, *Introductory Quantum Electrodynamics* (American Elsevier, New York, 1965), pp. 18–22.

[23]H. B. G. Casimir, Philips Res. Rep. 6, 162 (1951). The calculation is reproduced in a slightly extended version at the beginning of Ref. 19.

[24]L. S. Brown and G. J. Maclay, Ref. 5.

[25]See for example, *Handbook of Mathematical Functions*, edited by M. Abramowtiz and I. A. Stegun, NBS Appl. Math. Ser. 55 (U.S. GPO, Washington, D.C., 1965), p. 804.

[26]See Ref. 20, p. 36, Eq. (1.421 No. 4).

[27]See Ref. 20, p. 1073, Eq. (9.522 No. 1).

[28]See Ref. 20, p. 51, Eq. (1.643 No. 1).

[29]See Ref. 20, p. 1074, Eq. (9.542 No. 1); and p. 1076, Eq. (9.611 No. 2).

[30]F. London, Z. Phys. 63, 245 (1930); Z. Phys. Chem. B 11, 222 (1930).