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Finite-temperature corrections to the van der Waals potential

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We evaluate finite-temperature corrections to the two-photon exchange potential between polarizable systems. We find a complex (additive) correction of the form: $\operatorname{Re} V^T \sim 1/r$, $\operatorname{Im} V^T \sim \text{const}$, for $r<1/T$; and $\operatorname{Re} V^T \sim 1/r^6$, $\operatorname{Im} V^T \sim 1/r^6$, for $r>1/T$. These results are to be compared with the Feinberg-Sucher zero-temperature answer, $\operatorname{Re} V^{T=0} \sim 1/r^7$, $\operatorname{Im} V^{T=0} \equiv 0$.

I. INTRODUCTION

In 1968 and 1970,[1] Feinberg and Sucher studied the van der Waals interaction $V_{2\gamma}^{AB}(r)$ arising from two-photon exchange between neutral spinless systems A and B. They extended the result of Casimir and Polder[2] by showing that for separation r much larger than the size of either system, the potential has the form

$$V_{2\gamma}(r)=\frac{-1}{(4\pi)^3 r^7}\left[23\alpha_E^A\alpha_E^B+23\alpha_B^A\alpha_B^B -7\alpha_B^A\alpha_E^B-7\alpha_E^A\alpha_B^B\right], \tag{1}$$

where α_E and α_B are the electric and magnetic polarizability of the system. Recently there has been, for a variety of reasons, increasing interest in computing finite-temperature corrections to (zero-temperature) field-theory results.[3] For the most part, these calculations have required evaluation of one-loop corrections for fixed values of external momenta or for decay amplitudes. In computing the finite-temperature corrections to the van der Waals potential we encounter a somewhat richer exercise; we need to compute a finite-temperature one-loop scattering amplitude.

We follow the treatment of the zero-temperature case given in the book of Itzykson and Zuber.[4] They write

$$V(r)=i(2\pi)^{-3}(4m_a m_b)^{-1}\int d^3q\, e^{i\mathbf{q}\cdot\mathbf{r}}\mathscr{F}(q)\ , \tag{2}$$

where q is the momentum transfer, and the two-body scattering amplitude (for $a+b\to a'+b'$) $\mathscr{F}$ is given by

$$\mathscr{F}(q)=(2\pi)^{-4}\int\frac{d^4k\, d^4k'}{(k^2+i\epsilon)(k'^2+i\epsilon)}\times\delta^4(k+k'-q)d(k,k') \tag{3}$$

with $q=p_b-p_{b'}=p_{a'}-p_a$. $d(k,k')$ is given by[4]

$$d(k,k')=8g_2^a g_2^b K_{\mu\nu,\rho\sigma}(k)K^{\mu\nu,\rho\sigma}(k')+[4g_1^a g_2^b(p_\alpha^a p_\beta^{a'}+p_\beta^a p_\alpha^{a'})K^{\alpha\nu,\rho\sigma}(k)K^{\beta}{}_{\nu,\rho\sigma}(k')+(a\leftrightarrow b)] +g_1^a g_1^b[(p_\alpha^a p_\beta^{a'}+p_\beta^a p_\alpha^{a'})K^{\alpha\nu,\alpha'\sigma}(k)K^{\beta}{}_{\nu}{}^{\beta'}{}_{\sigma}(k')(p_{\alpha'}^b p_{\beta'}^{b'}+p_{\beta'}^b p_{\alpha'}^{b'})+(k\leftrightarrow k')]\ . \tag{4}$$

In (4) the tensor K, the propagator numerator for the field $F_{\mu\nu}$, is given by

$$K_{\mu\nu,\rho\sigma}=k_\mu k_\rho g_{\nu\sigma}-k_\nu k_\rho g_{\mu\sigma}-k_\mu k_\sigma g_{\nu\rho}+k_\nu k_\sigma g_{\mu\rho} \tag{5}$$

and (5) results from a phenomenological Hamiltonian density of the form

$$\mathscr{H}=g_1\partial_\alpha\phi\partial_\beta\phi F^{\alpha\gamma}F^{\beta}{}_{\gamma}+g_2\phi^2F^2 \tag{6}$$

with

$$g_1=\frac{\alpha_E+\alpha_B}{2m},\quad g_2=-\frac{m}{4}\alpha_B\ . \tag{7}$$

Using (2)–(5) Itzykson and Zuber[4] recapture the result of Feinberg and Sucher[1] of Eq. (1).

We modify the calculation of Eq. (3) by replacing the zero-temperature propagator $(k^2+i\epsilon)^{-1}=P(k)$ by its finite-temperature value

$$P^T(k)=\frac{1}{k^2+i\epsilon}-2\pi i\delta(k^2)(e^{|\mathbf{k}|/T}-1)^{-1} \tag{8}$$

and compute the corrections due to the extra term in $P^T(k)$ and $P^T(k')$.

Our calculations based on Eq. (4) in the real time formalism can be compared with those of Dzyaloshinski *et al.*[5] in the imaginary time formalism. These authors compute the temperature dependence of the van der Waals force between parallel plates in a dielectric medium. They find, for $rT\gg1$, a linear dependence on T, as we do. However, because the finite-temperature correction is isolated in (8) as an additive term, calculations in the real time formalism have the advantage of yielding the finite-temperature corrections explicitly.

It should be emphasized that our calculations are based solely on the correction of Eq. (8) to the photon propagator. Thus we omit several corrections of order T/m such as temperature corrections to fermion and composite particle propagators and corrections to photon particle vertices. We also consider only the van der Waals force between ground-state systems so that our results are only relevant for ensembles with $T/\Delta E$ less than, say, $\frac{1}{10}$, where ΔE is the lowest excited state.

This approximation allows us to base our calculations, as in Feinberg and Sucher[1] and Eq. (2) above, on polarizabilities coupled to the fields quadratically rather than products of transition dipole moments coupled to the fields linearly since the latter sum to the former with these approximations as shown in the original work of Casimir and Polder.[2] Finally, we note that we do not compute the (temperature-dependent) correction to the potential that arises from the nonzero velocity of the polarizable system.

II. CALCULATIONS

There are two kinds of corrections to (3) from the propagator (8). The real part of the finite-temperature potential $V^T(r)$ is modified by the cross term between the principal value of the first term in $P^T(k)$ and the second term in $P^T(k')$. The second effect is that $V^T(r)$ gains an imaginary contribution from the product of the finite-temperature parts of $P^T(k)$ and $P^T(k')$ plus the cross terms between the finite-temperature parts of (8) and the δ function from the first term in (8). We begin with the real part.

The correction to the real part of the potential is

$$\Delta V_R^T=\frac{1}{4m_a m_b(2\pi)^5 r}\times\int dq\,q\sin(qr)\int\frac{d^4k}{k^2}\delta(k'^2)n(\omega)d(k,k')\ , \tag{9}$$

where $k'=q-k$ and we have written $n(\omega)$ for

$$(e^{|\mathbf{k}|/T}-1)^{-1}=(e^{\beta\omega}-1)^{-1}\ .$$

In evaluating d in (9) we use the approximation $p=(m,\mathbf{0})$, for p_a, $p_{a'}$, p_b, and $p_{b'}$, and the approximation $q=(0,\mathbf{q})$. These approximations are equivalent to assuming that T is much less than m. We use the fact that

$$\int d^4k\,\delta(k'^2)=\frac{2\pi}{q}\int_0^\infty dk_0\int_{|k_0-q|}^{k_0+q}dk\,k\,\bigg|_{z=(q^2+k^2-k_0^2)/2kq}\ , \tag{10}$$

where z is the cosine of the angle between $\mathbf{k}$ and $\mathbf{q}$, $k=|\mathbf{k}|$ and $q=|\mathbf{q}|$, and $k^2=\mathbf{k}\cdot\mathbf{k}$ and $q^2=\mathbf{q}\cdot\mathbf{q}$. With this information (9) becomes

$$\begin{aligned}\Delta V_R^T=\frac{2}{4m_a m_b(2\pi)^4 r}\int dq\,q\sin(qr)\int_0^\infty dk_0\frac{1}{q}\int dk\frac{k}{k_0^2-k^2}n(\omega)\\ \times\{q^4[8g_2^a g_2^b+2(m_a^2 g_1^a g_2^b+m_b^2 g_1^b g_2^a)+m_a^2 m_b^2 g_1^a g_1^b]\\ +4m_a^2 m_b^2 g_1^a g_1^b k_0^2(2k_0^2-q^2)\}\ .\end{aligned} \tag{11}$$

In writing (11) we have used the fact that terms in d proportional to k^2 result in contributions to ΔV_R^T of the form $\int_0^\infty dq\,q^{2n+1}\sin(qr)$ and hence vanish. Equation (11) can be evaluated in closed form with the help of two Fourier sine transforms[6]

$$\int_0^\infty dx\sin(xy)\ln\left|\frac{x+a}{x-a}\right|=\frac{\pi}{y}\sin(ay)\ , \tag{12}$$

$$\int_0^\infty dx\frac{\sin(xy)}{e^{ax}-1}=\frac{\pi}{2a}\coth\left[\frac{\pi y}{a}\right]-\frac{1}{2y}\ . \tag{13}$$

Using these results we have

$$\Delta V_R^T=-8\frac{T}{r}\left[AD^4+\tfrac{1}{16}B\frac{1}{r}D^4r+\tfrac{1}{4}BD^2\frac{1}{r}D^2r\right]\times\frac{1}{r}\left[\frac{\pi}{2}\coth\left[\frac{2\pi r}{\beta}\right]-\frac{\beta}{4r}\right]\ , \tag{14}$$

where we have written $D=d/dr$ and defined

$$A=\frac{1}{4m_a m_b(2\pi)^3}\times[8g_2^a g_2^b+2m_a m_b(g_1^a g_2^b+g_2^a g_1^b)+m_a^2 m_b^2 g_1^a g_1^b] \tag{15}$$

and

$$B=\frac{1}{4(2\pi)^3}m_a m_b g_1^a g_1^b\ . \tag{16}$$

Using the well-known expansion

$$\coth x=\frac{1}{x}\left[1+\frac{x^2}{3}-\frac{x^4}{45}+\frac{2x^6}{945}+\cdots\right] \tag{17}$$

we have, for $rT\ll 1$,

$$\Delta V_R^T=\frac{-8\pi(2\pi)^5}{945}\frac{T^6}{r}(24A+\tfrac{35}{2}B)\ . \tag{18}$$

For $rT\gg 1$, (14) becomes

$$\Delta V_R^T=\frac{-96\pi T}{r^6}\ . \tag{19}$$

Comparing with (1), one sees that $V_R^T/V_{2\gamma}^{T=0}$ is of the order rT for large T; it is not suppressed by any factors of T/m. Also, the sign of the finite-temperature contribution is the same as that of the $T=0$ contribution for all values of rT.

The imaginary part of ΔV^T can be similarly evaluated:

$$\Delta V_I^T = \frac{-1}{2m_a m_b r(2\pi)^4} \times \int_0^\infty dq\, q\sin(qr) \times \int d^4k\, \delta(k^2)\delta(k'^2) \times n(\omega)[n(\omega)+1]d(k,k') . \tag{20}$$

In the nonrelativistic limit, we have

$$d = 8m_a m_b (2\pi)^3 q^4[A+4B(2y^4-y^2)] , \tag{21}$$

with A and B as given in (15) and (16) and where $y=k/q$. Substituting (21) into (20) gives

$$\Delta V_I^T = -\frac{1}{r}(AK_0+8BK_4-4BK_2) , \tag{22}$$

where

$$K_n = \int_0^\infty dq \sin(qr) q^5 \int_{1/2}^\infty dy \frac{e^{\beta qy}}{(e^{\beta qy}-1)^2} y^n . \tag{23}$$

We are able to obtain an analytic expression only for the case $n=0$. It is

$$K_0 = \frac{1}{\beta} D^4 \left[\frac{\pi}{\beta} \coth\left[\frac{2\pi r}{\beta}\right] - \frac{1}{2r} \right] . \tag{24}$$

In the region where $rT \ll 1$, (24) implies

$$K_0 \sim -\tfrac{8}{63}(2\pi)^6 rT^7 . \tag{25}$$

In this limit the $n=2$ and $n=4$ contributions are negligible since

$$K_n = -\frac{d}{d\beta}\left[\frac{d}{dr}\right]^4 \int_{1/2}^\infty dy\, y^{n-1} \int_0^\infty dq \frac{\sin(qr)}{e^{\beta qy}-1} \sim \mathcal{O}(rT^7(rT)^n) . \tag{26}$$

For $rT \gg 1$,

$$K_0 \sim -\frac{12}{\beta r^5} \tag{27}$$

and, by changing to a new variable $u=r/\beta y$, the $n=2$ and $n=4$ contributions are again small:

$$K_n = -\frac{d}{d\beta}\frac{1}{\beta^n}\frac{d^4}{dr^4} r^{n-1} \int_0^{2r/\beta} \frac{du}{u^n} \left[\frac{\pi}{2} - \frac{1}{4u} + \frac{\pi e^{-2\pi u}}{1-e^{-2\pi u}} \right] = \mathcal{O}(e^{-4\pi r/\beta}) . \tag{28}$$

Therefore in both limiting cases, we have the general expression

$$\Delta V_I \approx -\frac{A}{r} K_0 . \tag{29}$$

For $rT \ll 1$, this gives

$$\Delta V_I^T = \tfrac{8}{63}(2\pi)^6 AT^7 , \tag{30}$$

and for $rT \gg 1$,

$$\Delta V_I^T = \frac{12AT}{r^6} . \tag{31}$$

Thus for $rT \ll 1$, ΔV_I^T is suppressed compared to ΔV_R^T by a factor of rT. For $rT \gg 1$, the temperature and r dependence of ΔV_I^T is the same as that of ΔV_R^T; the imaginary part is suppressed by only a factor of 8π.

We also consider briefly the force between a charged particle and a spinless neutral particle. The $T=0$ value has been computed by Feinberg and Sucher;[7] they obtain from the two-photon exchange a potential

$$V_{2\gamma}(r) = \frac{\alpha\alpha_E}{2r^4} \tag{32}$$

for $r > r_B$ (r_B denotes the Bohr radius). The temperature-dependent corrections to this potential can be computed with the procedure used above for two neutral particles. However, in this case there is a lower-order (tree) diagram in which only one photon couples to the charged particle while the second is absorbed or emitted by the heat bath. The contribution for photon absorption by the heat bath is

$$T(p_1+p_2\to p_3+p_4) = \frac{eg_1}{q^2}(p_1+p_3)^\lambda(p_4^\alpha p_2^\beta + p_4^\beta p_2^\alpha)[(k_\alpha\epsilon_\rho - k_\rho\epsilon_\alpha)(q_\rho g_{\beta\lambda} - q_\beta g_{\rho\lambda}) + (\alpha\leftrightarrow\beta)] - \frac{4eg_2}{q^2}(p_3+p_1)_\alpha(k_\mu\epsilon_\nu - k_\nu\epsilon_\mu)[(p_1-p_3)^\mu g^{\nu\alpha} - (p_1-p_3)^\nu g^{\mu\alpha}] , \tag{33}$$

where we have used the momentum transfer $q=p_1-p_3$ and the momentum of the absorbed photon $k=p_1+p_2-p_3-p_4$. From (33) we computed the differential cross section for the one-γ exchange process

$$\left.\frac{d\sigma}{dq^2}\right|_{1\gamma} = -\frac{\alpha}{6\pi^2}\frac{1}{p_1^2 q^2}[\alpha_E^2 E_1^2 + \alpha_B^2(p_1^2+\tfrac{1}{4}q^2)] \times \int_0^{E_1-m} d\omega\,\omega^3 \left[1+\frac{1}{e^{\omega/T}+1}\right] , \tag{34}$$

where m, E_1, and p_1 are the mass, energy, and 3-momentum of the charged particle. The integral can be done explicitly in the limits $E_1-m \gg T$ and $E_1-m \ll T$ with the result

$$\int_0^{E_1-m} d\omega\,\omega^3[1+(e^{\omega/T}+1)^{-1}] = \begin{cases} \frac{1}{4}(E_1-m)^4\left[1+\frac{4\pi^4}{15}\frac{T^4}{(E_1-m)^4}\right], & T \ll E_1-m \\ \frac{1}{4}(E_1-m)^4\left[1+\frac{4}{3}\frac{T}{(E_1-m)}\right], & T \gg E_1-m\ . \end{cases} \tag{35}$$

To compare, we see that (32) gives a differential cross section

$$\left.\frac{d\sigma}{dq^2}\right|_{2\gamma} = \frac{\alpha^2\alpha_E^2}{(2\pi)^6}\frac{E_1^2}{8p_1^2q^2r_B^2} \times \left[\sin(qr_B)+qr_B\cos(qr_B)-q^2r_B^2\frac{\pi}{2}\right]^2 , \tag{36}$$

where we have cut off the divergent r integral at the Bohr radius r_B.

The ratio R, at $T=0$, of $(d\sigma/dq^2)\,|_{2\gamma}$ to the α_E term in $(d\sigma/dq^2)\,|_{1\gamma}$ is

$$R=\frac{3}{4}\frac{\alpha}{(2\pi)^4}\frac{1}{r_B^4(E_1-m)^4} \times \left[\sin(qr_B)+qr_B\cos(qr_B)-q^2r_B^2\frac{\pi}{2}\right]^2 . \tag{37}$$

R is less than one only for E_1-m greater than about 100 eV. Thus this one-photon exchange effect is small in, for example, electron-atom scattering for E_1-m below ionization energies. By detailed balance the process where the photon is emitted by the heat bath gives the same result.

III. DISCUSSION

We interpret the fact that the finite-temperature correction to the potential between neutral, spinless, polarizable systems falls off less rapidly than the $T=0$ van der Waals potential (r^{-6} versus r^{-7}) as a reflection of the fact that the heat bath can play a role in polarizing the neutral particles. Similarly, the heat bath produces an imaginary part in the potential at energies below the excitation energies of systems A and B because it can absorb (or provide) energy in the scattering process.

Applications of our results to physical scattering processes are not immediate. Van der Waals forces are not observed in scattering processes directly. The finite-temperature correction will dominate the $T=0$ force for $rT>1$. For an ideal atomic gas we must require $T\lesssim 1$ eV since above this energy ionization processes and excited states become increasingly important. For $T\sim 1$ eV the correction is important for $r\gtrsim 10^{-5}$ cm; this corresponds to interatomic spacing in gases with densities on the order of 10^{-6} atmospheric densities.

Connection between the van der Waals force and experiment is provided by the virial coefficients of gases. Experimental data on the equation of state of a gas are generally fitted to a polynomial in the density ρ obtained by truncating the so-called virial series:

$$\beta\frac{P}{\rho}=\sum_{n=1}^{\infty}B_n(T)\rho^{n-1} ,$$

where P is the pressure and B_n is the nth virial coefficient. By convention one writes $B_1=1$, corresponding to ideal gas behavior. The second virial coefficient $B_2(T)$ incorporates deviations from this. In one low-density approximation it is given by

$$B_2(T)=-2\pi\int_0^{\infty}dr\,r^2\{\exp[-\beta V(r)]-1\} .$$

For a complex potential $V^T(r)$ at finite temperature, we might modify this expression by replacing $V(r)$ by $|V(r)+V^T(r)|$ and attempt a measurement of $B_2(T)$ as a function of temperature to explore the temperature dependence of $V(r)$.

We do not consider it too likely that deviations from the ideal gas law are easily studied for gases at 10^4 K at such low densities; at higher densities or lower temperatures the scattering would be sensitive only to the shorter range part of the potential for which the $T=0$ potential dominates.

Another possibility for observing experimentally the van der Waals force and its temperature-dependent corrections is to look at large aggregates of matter. Since the van der Waals potential goes as N_1N_2, where N_i is the number of polarizable atoms in the ith aggregate, it dominates the gravitational potential for r small enough—on the order of, or less than, 0.01 cm. Happer has emphasized[8] the fact that experiments potentially sensitive to the van der Waals force could be performed using neutral colloidal suspensions in water or other solvents. Such experiments could well be capable of detecting temperature-dependent corrections.

A third place to consider possible corrections would be in astrophysics. If we view the nucleon-nucleon potential as a van-der-Waals-like effect of a quark-quark potential in color singlet states, we can estimate the temperature and densities at which temperature could be important. Since the nuclear force falls sharply for $r>10^{-13}$ cm, we expect the correction to be significant only for temperatures approaching 100 MeV. They should thus be negligible at the time of cosmic nucleosynthesis where $T\sim 0.1$ MeV. However, in supernova temperatures rise to 10 MeV or more. It is therefore possible that nuclear cross sections in supernova are significantly different from the $T=0$ cross sections. Van der Waals calculations at zero temperature have also been done in the context of composite models of quarks and leptons,[9] but the model Hamiltonian of Eq. (6) does not support quantitative estimates of these effects.

This elusiveness of finite-temperature correction in the present problem is similar to other cases[10] in which this theoretically interesting effect has minimal practical significance.

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