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Long-range Casimir-Polder-Feinberg-Sucher intermolecular potential at nonzero temperature

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A simple Hamiltonian determines in closed form the potential of the long-range force between two fixed molecules polarizable magnetically as well as electrically, exposed to blackbody radiation at temperature T. The results apply provided $kT \ll \hbar\Omega$ and at separations $\rho \gg c/\Omega$, with $\hbar\Omega$ a typical molecular excitation energy.

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I. INTRODUCTION AND CONCLUSIONS

From the work of Casimir and Polder, one is familiar with the fact that at separations $\rho = |\mathbf{r}_A - \mathbf{r}_B|$ well above typical absorption wavelengths $2\pi c/\Omega$, and at zero temperature, the potential W between two neutral molecules A and B fixed at $\mathbf{r}_{A,B}$, with electrostatic polaribilities [1] $\alpha_{A,B}$, is given by

$$W_{CP}(T=0) = -\alpha_A\alpha_B \frac{23\hbar c}{4\pi\rho^7}. \tag{1}$$

Allowing for magnetic polarizabilities $\chi_{A,B}$, Feinberg and Sucher [2] and Boyer [3] found

$$W(T=0) \equiv \frac{\hbar c}{4\pi\rho^7}\{-23(\alpha_A\alpha_B + \chi_A\chi_B) + 7(\alpha_A\chi_B + \chi_A\alpha_B)\}. \tag{2}$$

For references and accessible discussions, see, e.g., Boyer [3], Power [4], and Sucher and Feinberg [5].

Here we consider only the idealized case where α and χ are nondispersive (i.e., strictly independent of frequency): our object is to generalize Eq. (2) to nonzero temperature, i.e., to molecules immersed in blackbody radiation at temperature $T > 0$, supplementing the restriction $\rho\Omega/c \gg 1$ with $kT \ll \hbar\Omega$, which effectively confines each molecule to its ground state. The results are useful, for instance, in perturbative calculations of the Casimir shifts of molecular solids (where $A = B$), electromagnetically dilute in the sense that both ε and μ are close to unity. The nondispersive shifts thus determined are reported in the following paper [6] (cited as IV), drawing on the general theory developed elsewhere [7,8] (cited as II and V) for dispersive media at $T=0$ and $T>0$.

With $\chi_A = \chi_B = 0$, the result is well known (see, e.g., McLachlan [9], Boyer [10], and appropriate limits from Goedecke and Wood [11]):

$$W_{CP}(T) = -\alpha_A\alpha_B \frac{kT}{\rho^6} Q \coth(2\pi kT\rho), \tag{3}$$

featuring the zero-degree homogeneous differential operator

$$Q \equiv 3 - 3\rho\partial + \frac{5}{4}\rho^2\partial^2 - \frac{1}{4}\rho^3\partial^3 + \frac{1}{16}\rho^4\partial^4, \quad \partial \equiv \frac{\partial}{\partial\rho}. \tag{4}$$

Equation (3) is rederived in Sec. II. Given

$$\coth(z\to 0) = \frac{1}{z} + \frac{z}{3} - \frac{z^3}{45} + \frac{2z^5}{945} - \frac{z^7}{4725} + \cdots, \tag{5}$$

and

$$\coth(z\to\infty) = 1 + 2\{\exp(-2z) + \exp(-4z) + \cdots\}, \tag{6}$$

it is easy to verify that, to leading order, $W_{CP}(2\pi kT\rho/\hbar c \ll 1)$ reduces to Eq. (1), while

$$W_{CP}(2\pi kT\rho/\hbar c \gg 1) \simeq -\alpha_A\alpha_B \frac{3kT}{\rho^6}. \tag{7}$$

Section II generalizes these expressions to molecules polarizable magnetically as well as electrically. It starts from a very simple Hamiltonian and routes the calculation so that two of the crucial intermediate results can (in the Appendix) be adapted almost directly from the classic text by Lifshitz and Pitaevskii [12] (their expressions suffice to deal also with anisotropic polarizabilities, which here we exclude for simplicity). Section III specializes the results to $\chi = -\alpha$, appropriately to dilute materials with unit refractive index, i.e., with $\varepsilon\mu = 1$. This scenario, introduced by Brevik and Kolbenstvedt [13], often attracts field theorists considering Casimir energies (some recent references are given in IV).

Our end result for the potential is given in closed form by Eq. (15) in terms of the two auxiliary functions (19) and (22) whose asymptotics for $2\pi kT\rho/\hbar c$ small or large are displayed in Eqs. (23)–(26). It is noteworthy, and unexpected, that at large distances the electric-magnetic cross terms diminish exponentially faster than the pure electric and pure magnetic contributions.

II. NONDISPERSIVE POTENTIAL

The twin restrictions we have imposed amount to disregarding dispersion, and are validated formally by taking the *nondispersive limit* $\Omega \to \infty$ from the outset. In realistic cases (where generally $|\chi| \ll \alpha$), it is not too difficult to allow for finite Ω [9,11], but it would become very awkward to do so when χ is not negligible, if only because magnetic and dielectric contributions disperse so differently (see Power [4], Farina *et al.* [14], and Salam [15]). On the other hand, the

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nondispersive regime is covered by the very simple Hamiltonian

$$H=H_{\rm rad}+H_{\rm int}, \quad H_{\rm int}=H_{\rm int}(A)+H_{\rm int}(B), \tag{8}$$

where $H_{\rm rad}$ is the Hamiltonian for the free Maxwell field,

$$H_{\rm int}(A)=-\frac{1}{2}\{\alpha_A\mathbf{E}^2(\mathbf{r}_A)+\chi_A\mathbf{B}^2(\mathbf{r}_A)\}, \tag{9}$$

and similarly for $H_{\rm int}(B)$. It is from just this Hamiltonian that Eq. (2) was first derived by Feinberg and Sucher [2].

The potential $W(T)$ we require consists of parts of the shift $\Delta^{(2)}F$ in the Helmholtz free energy of the system (radiation plus molecules A and B) *of second order in* $H_{\rm int}$: namely, the parts that depend on the presence of both molecules, and are proportional to any product [16] of α_A or χ_A with α_B or χ_B. It is these free-energy shifts that give the intermolecular force as $-\boldsymbol{\nabla}_\rho W$. To keep track of factors of 2, it helps to start by writing down the result at $T=0$, namely, the familiar second-order shift of the (ordinary) energy, expressible as

$$\begin{aligned}\Delta^{(2)}\mathcal{E}&=\frac{1}{2}\{\langle 0|H_{\rm int}|1\rangle+\langle 1|H_{\rm int}|0\rangle\}\\ &=\frac{1}{2}\{\langle|H_{\rm int}|\rangle-(\text{diagonal terms})\},\end{aligned} \tag{10}$$

where $|\rangle=|0\rangle+|1\rangle$, with $|0\rangle$ the zero-order ground state (no photons) and $|1\rangle$ the first-order correction [two photons both generated either by $H_{\rm int}(A)$ or $H_{\rm int}(B)$].

Thermodynamic perturbation theory (see, e.g., Landau and Lifshitz [17] and Peierls [18]) then prescribes W as the appropriate part of the expectation value formed from correspondingly perturbed canonical averages $\langle\cdots\rangle$. Three enormous simplifications yield W almost at once.

First, we are dealing only with the degrees of freedom of the Maxwell field: the nondispersive limit has eliminated the internal dynamics of the molecules.

Second, one finds straightforwardly that

$$W(T)=-\frac{1}{2}\alpha_A\langle\mathbf{E}^2(B\to A)\rangle-\frac{1}{2}\chi_A\langle\mathbf{B}^2(B\to A\rangle, \tag{11}$$

where $\langle\mathbf{E}^2(B\to A)\rangle$ and $\langle\mathbf{B}^2(B\to A)\rangle$ are the expectation values, at molecule A, of the squared E and B fields due to the oscillating dipoles (both electric and magnetic) induced in molecule B by the randomly fluctuating fields (zero point plus thermal) acting on it. Here the prefactor of 1/2 from Eq. (10) has been canceled [19] by a factor of 2, allowing for the reciprocal effect of molecule B experiencing the fields of the fluctuating dipoles induced in molecule A.

Next, subdivide

$$\langle\mathbf{E}^2(B\to A)\rangle=\alpha_B\langle\mathbf{E}^2(ee)\rangle+\chi_B\langle\mathbf{E}^2(em)\rangle \tag{12}$$

into contributions from the electric and magnetic dipoles induced in molecule B, and subdivide $\langle\mathbf{B}^2(B\to A)\rangle$ analogously:

$$\begin{aligned}W(T)=&-\frac{1}{2}\alpha_A\langle\{\alpha_B\mathbf{E}^2(ee)+\chi_B\mathbf{E}^2(em)\}\rangle\\ &-\frac{1}{2}\chi_A\langle\{\alpha_B\mathbf{B}^2(me)+\chi_B\mathbf{B}^2(mm)\}\rangle.\end{aligned} \tag{13}$$

Since the symmetries of the Maxwell field and blackbody radiation entail

$$\langle\mathbf{E}^2(ee)\rangle=\langle\mathbf{B}^2(mm)\rangle, \quad \langle\mathbf{E}^2(em)\rangle=\langle\mathbf{B}^2(me)\rangle, \tag{14}$$

Eq. (13) reduces to

$$\begin{aligned}W(T)=&-\frac{1}{2}(\alpha_A\alpha_B+\chi_A\chi_B)\langle\mathbf{E}^2(ee)\rangle-\frac{1}{2}(\alpha_A\chi_B+\chi_A\alpha_B)\\ &\times\langle\mathbf{E}^2(em)\rangle.\end{aligned} \tag{15}$$

To save writing, from here on we take the two molecules to be identical, further reducing Eq. (15) to

$$W(T)=-\frac{1}{2}(\alpha^2+\chi^2)\langle\mathbf{E}^2(ee)\rangle-\alpha\chi\langle\mathbf{E}^2(em)\rangle. \tag{16}$$

Third, our most providential simplification is that some straightforward manipulations, spelled out in the Appendix, link the Fourier transforms of the two canonical averages in Eqs. (15) and (16) to the corresponding results for vector potentials already worked out by Lifshitz and Pitaevskii [12]. For brevity, we define

$$\begin{aligned}\langle\mathbf{E}^2(ee)\rangle_\omega\equiv\int_{-\infty}^{\infty}dt\exp(i\omega t)\,\frac{1}{2}\langle E_l(\mathbf{r}_A,t)E_l(\mathbf{r}_A,0)\\ +E_l(\mathbf{r}_A,0)E_l((\mathbf{r}_A,t)\rangle\end{aligned} \tag{17}$$

and other such transforms similarly. Then one finds

$$\langle\mathbf{E}^2(ee)\rangle_\omega=\frac{2}{\rho^6}\coth\left(\frac{\omega}{2kT}\right)Q\sin(2\omega\rho), \tag{18}$$

whence

$$\langle\mathbf{E}^2(ee)\rangle=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\langle\mathbf{E}^2(ee)\rangle_\omega=\frac{2kT}{\rho^6}Q\coth(2\pi kT\rho). \tag{19}$$

Similarly, one finds

$$\langle\mathbf{E}^2(em)\rangle_\omega=-\frac{2}{\rho^6}\coth\left(\frac{\omega}{2kT}\right)P\sin(2\omega\rho), \tag{20}$$

where

$$P\equiv\frac{1}{4}\rho^2\partial^2-\frac{1}{4}\rho^3\partial^3+\frac{1}{16}\rho^4\partial^4. \tag{21}$$

Thus

$$\langle \mathbf{E}^2(em)\rangle = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\langle \mathbf{E}^2(em)\rangle_\omega = -\frac{2kT}{\rho^6}P\coth(2\pi kT\rho). \tag{22}$$

The asympotics of $\langle \mathbf{E}^2(ee)\rangle$ and $\langle \mathbf{E}^2(em)\rangle$ are found by acting on Eqs. (5) and (6) with Q and P. For $2\pi kT\rho \ll 1$, one obtains

$$\langle \mathbf{E}^2(ee)\rangle = \frac{23}{2\pi\rho^7} + \frac{22(2\pi)^5}{945}\frac{(kT)^6}{\rho} + O((kT)^8\rho), \tag{23}$$

$$\langle \mathbf{E}^2(em)\rangle = -\frac{7}{2\pi\rho^7} + \frac{10(2\pi)^5}{945}\frac{(kT)^6}{\rho} + O((kT)^8\rho), \tag{24}$$

where the manifest gaps reflect the relations $Q\rho = P\rho = Q\rho^3 = P\rho^3 = 0$. For $2\pi kT\rho \gg 1$, one obtains

$$\langle \mathbf{E}^2(ee)\rangle = \frac{kT}{\rho^6}\{6 + 4Q\exp(-4\pi kT\rho) + O\exp(-8\pi kT\rho)\}, \tag{25}$$

$$\langle \mathbf{E}^2(em)\rangle = \frac{kT}{\rho^6}\{-4P\exp(-4\pi kT\rho) + O\exp(-8\pi kT\rho)\}. \tag{26}$$

The reason why $\langle \mathbf{E}^2(em)\rangle$ vanishes exponentially fast at large separations is that, unlike Q, the operator P has no components free of $\partial/\partial\rho$, whence it totally destroys the leading term $+1$ on the right of Eq. (6).

III. SPECIAL CASE $\chi = -\alpha$

Finally, we assemble the results for the special case mentioned in Sec. I. With $\chi = -\alpha$, substitution into Eq. (16) from Eqs. (19) and (22) yields

$$W = -\alpha^2\frac{2kT}{\rho^6}R\coth(2\pi kT\rho), \tag{27}$$

where

$$R = Q + P = 3 - 3\rho\partial + \frac{3}{2}\rho^2\partial^2 - \frac{1}{2}\rho^3\partial^3 + \frac{1}{8}\rho^4\partial^4. \tag{28}$$

Accordingly,

$$W(2\pi kT\rho \ll 1) = -\alpha^2\left\{\frac{15}{\pi\rho^7} + \frac{12(2\pi)^5}{945}\frac{(kT)^6}{\rho} + O((kT)^8\rho)\right\}, \tag{29}$$

$$W(2\pi kT\rho \gg 1) = -\alpha^2\frac{kT}{\rho^6}\{6 + 4R\exp(-4\pi kT\rho) + O\exp(-8\pi kT\rho)\}. \tag{30}$$

The reason why the leading term of Eq. (30) is just double the pure dielectric result (7) is that the (*mm*) contribution is the same as the (*ee*), while Eq. (26) shows that the (*em*) and (*me*) cross terms vanish much faster.

Note added in proof. In fact, an attempt to determine $W(T)$ is already on record; see Ref. [20].

APPENDIX: THE CANONICAL AVERAGES $\langle E^2(ee)\rangle$ AND $\langle E^2(em)\rangle$

We determine the expectation values needed in Eqs. (15) and (16). The results, transcribed into our own notation, are all cited from Lifshitz and Pitaevskii [12], referred to as LP. They apply in the dipole approximation and are derived in a gauge where $A_0 = 0$, so that $\mathbf{E} = -\dot{\mathbf{A}}$ and $\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A}$.

For the vector potential due to the electric polarizability of molecule B, LP's Sec. 77, problem 1, Eq. (1), with $\mathbf{R} \equiv \mathbf{s} - \mathbf{r}_B$ and $\mathbf{R}' \equiv \mathbf{s}' - \mathbf{r}_B$, yields the Fourier transform [defined analogously to Eq. (17)]

$$\langle A_i(\mathbf{s})A_k(\mathbf{s}')\rangle_\omega^{(e)} = \omega^2\coth(\omega/2kT)\,\mathrm{Im}\,D^R_{il}(\omega,R)D^R_{lk}(\omega,R'); \tag{A1}$$

with their Eq. (77.6) corrected for an obvious misprint, the retarded Green's tensor reads

$$D^R_{il}(\omega,R) = -\left\{\delta_{il} + \frac{1}{\omega^2}\partial^2_{il}\right\}Y, \quad Y \equiv \frac{\exp(i\omega R)}{R}. \tag{A2}$$

Performing the differentiations, one obtains

$$D^R_{il}(\omega,R) = -Y\{\delta_{il}h + \hat{R}_i\hat{R}_l g\}, \tag{A3}$$

where the carets specify unit vectors, and

$$h \equiv 1 + \frac{i}{\omega R} - \frac{1}{\omega^2R^2}, \quad g \equiv -1 - \frac{3i}{\omega R} + \frac{3}{\omega^2R^2}. \tag{A4}$$

Now use $\langle E_i(\mathbf{s})E_l(\mathbf{s}')\rangle_\omega = \omega^2\langle A_i(\mathbf{s})A_l(\mathbf{s}')\rangle_\omega$, set $\mathbf{s} = \mathbf{s}' = \mathbf{r}_A$ (whence $\mathbf{R} = \mathbf{R}' = \boldsymbol{\rho}$), and substitute from Eqs. (A3) and (A4) into Eq. (A1) to find the expression for $\langle \mathbf{E}^2(ee)\rangle_\omega$ already quoted in Eq. (18).

For the vector potential due to the magnetic polarizability of molecule B, LP's Sec. 77, problem 2, Eq. (2) plus their Eq. (76.6) yields similarly that

$$\begin{aligned}\langle A_i(\mathbf{s})A_i(\mathbf{s}')\rangle_\omega^{(m)} &= \coth(\omega/2kT)\,\mathrm{Im}\{\varepsilon_{ipl}\partial_p Y(R)\varepsilon_{lqi}\partial'_q Y(R')\}\\ &= 2\coth(\omega/2kT)\,\mathrm{Im}\{\boldsymbol{\nabla}Y(R)\cdot\boldsymbol{\nabla}'Y(R')\},\end{aligned} \tag{A5}$$

where the first line has reexpressed LP's somewhat peculiar operators curl in conventional language. On setting $\mathbf{s} = \mathbf{s}' = \mathbf{r}_A$ as before, straightforward manipulation leads to the expression for $\langle \mathbf{E}^2(em)\rangle_\omega$ already quoted in Eq. (20).

[1] We use natural units $\hbar = 1 = c$ (except for occasional emphasis) and unrationalized Gaussian units for the Maxwell fields. With rationalized units (and the standard rationalized definitions of α and χ), all our potentials W must be divided by $(4\pi)^2$, because they are due to two-photon exchange.

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[19] The writer often finds it difficult to see how such counting problems have been resolved even in the undoubtedly correct pioneering discussions, along similar lines, of the far more demanding dispersive case (e.g., [11]). Here we observe that these questions become appreciably more transparent if one can start from the Hamiltonian (8).

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