Negative Casimir Entropies in Nanoparticle Interactions

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Introduction

For more than a decade there has been a controversy surrounding entropy in the Casimir effect. This is most famously centered around the issue of how to describe a real metal, in particular, the permittivity at zero frequency. The latter determines the low-temperature and high temperature corrections to the free energy, and hence to the entropy.

Drude vs. plasma

The Drude model, and general thermodynamic and electrodynamic arguments, suggest that the transverse electric (TE) reflection coefficient at zero frequency for a good, but imperfect metal, should vanish, while an ideal metal, or one described by the plasma model (which ignores dissipation) has this zero frequency reflection coefficient equal unity.

3rd Law not violated

Taken at face value, the first, more realistic scenario, means that the entropy would not vanish at zero temperature, in violation of the Nernst heat theorem, and the third law of thermodynamics. However, subsequent careful calculations showed that at very low temperature the free energy vanishes quadratically in the temperature, thus forcing the entropy to vanish at zero temperature.

Negative entropy?

However, there would persist a region at low temperature in which the entropy would be negative. This was not thought to be a problem, since the Casimir free energy does does not describe the entire system of the Casimir apparatus, whose total entropy must necessarily be positive. The physical basis for the negative entropy region remains mysterious.

Geometric negative entropy

More recently, negative entropy has been discovered in purely geometrical settings. Thus, in considering the free energy between a perfectly conducting plate and a perfectly conducting sphere, it was found that when the distance between the plate and the sphere is sufficiently small, the room-temperature entropy turns negative, and that the effect is enhanced for smaller spheres. For a very small sphere, we can use a dipole approximation.

Systematic study

The previous discussion suggests that this phenomenon should be studied in a systematic way. In this talk we consider the retarded Casimir-Polder interactions between a small object, such as a nanosphere or nanoparticle, possessing anisotropic electric and magnetic polarizabilities, and a conducting plate, and we analyze the contributions to the free energy and entropy for the TE and TM (transverse magnetic) polarizations of the conducting plate.

Conducting sphere

The case of a small conducting sphere above a plate is recovered by setting the electric polarizability, α, equal to a^3, where a is the radius of the sphere, and the magnetic polarizability, β, equal to $-a^3/2$. We also examine the free energy and entropy between two such anisotropically polarizable nanoparticles.

Findings

We find negative entropy not only as an interplay between TE and TM polarizations in the plate, but even between a purely electrically polarizable nanoparticle and the TM polarization of the plate, provided the nanoparticle is sufficiently anisotropic. The previous negative entropy results are verified, and we show that even between electrically polarizable nanoparticles, negative entropy occurs when the product of the temperature with the separation is sufficiently small, provided the nanoparticles are sufficiently anisotropic. The interaction between two identical isotropic small spheres modeled as perfect conductors gives a negative entropy region, but not when they are described by the Drude model (no magnetic polarizability); but the interaction between an isotropic perfectly conducting sphere and an isotropic Drude sphere gives negative entropy. At room temperature, typically negative entropy occurs for separations below a few microns.

History

Negative entropy between an electrically polarizable atom and a conducting plate was discussed in the isotropic case several years ago by Mostepanko et al. (2008) who also sketched the extension to a isotropic magnetically polarizable atom (2009). The zero-temperature Casimir-Polder interaction between atoms having both isotropic electric and magnetic polarizabilities was studied by Feinberg and Sucher (1968).

History (cont.)

The temperature dependence for isotropic atoms interacting only through their electric polarizability was first obtained by McLachlan (1963). Barton performed the generalization for the magnetic polarizability at finite temperature (2001). Haakh et al. more recently discussed the magnetic Casimir-Polder interaction for real atoms (2009). The anisotropic case at zero temperature for the electrical Casimir-Polder interaction was first given by Craig and Power (1969).

Outline

In this paper we consider anisotropic small objects, with the symmetry axis of the objects coinciding with the direction between them or the normal to the plate, with both electric and magnetic polarizability. Because we are interested in matters of principle, we work in the static approximation, so both polarizabilities are regarded as constant, whereas most real atoms have very small, and complicated, magnetic polarizabilities.

Advantage of nanoparticles

We also are not concerned here with the fact that achieving large anisotropies is likely to be difficult for real atoms because it may be much more feasible to achieve the necessary anisotropies with nanoparticles, such as conducting needles. We use natural units $\hbar = c = k_B = 1$, and Heaviside-Lorentz units for electrical quantities, except that polarizabilites are expressed in conventional Gaussian units.

CP free energy: nanoparticle/plate

We start by considering an anisotropic electrically and magnetically polarizable nanoparticle a distance Z above a perfectly conducting plate. We can take as our starting point the multiple scattering formula for the interaction free energy between two bodies

$$F_{12} = \frac{1}{2}\operatorname{Tr}\ln(\mathbf{1} - \boldsymbol{\Gamma}_0 \mathbf{T}_1^E \boldsymbol{\Gamma}_0 \mathbf{T}_2^E) + \frac{1}{2}\operatorname{Tr}\ln(\mathbf{1} - \boldsymbol{\Gamma}_0 \mathbf{T}_1^M \boldsymbol{\Gamma}_0 \mathbf{T}_2^M) - \frac{1}{2}\operatorname{Tr}\ln(\mathbf{1} + \boldsymbol{\Phi}_0 \mathbf{T}^E \boldsymbol{\Phi}_0 \mathbf{T}^M),$$

Green's dyadic

where the Γ_0 is the free electric Green's dyadic,

$$\mathbf{\Gamma}_0(\mathbf{r},\mathbf{r}') = (\boldsymbol{\nabla}\boldsymbol{\nabla} - \mathbf{1}\nabla^2)G_0(|\mathbf{r}-\mathbf{r}'|), \quad G_0(R) = \frac{e^{-|\zeta|R}}{4\pi R},$$

in terms of the imaginary frequency ζ. The auxilliary Green's dyadic is

$$\mathbf{\Phi}_0 = -\frac{1}{\zeta}\boldsymbol{\nabla}\times\mathbf{\Gamma}_0.$$

$\mathbf{T}_{1,2}^{E,M}$ are the electric and magnetic scattering operators for the two interacting bodies.

Single scattering approximation

For the case of a tiny object, it suffices to use the single-scattering approximation, and replace the scattering operator by the potential

$$\mathbf{T}_n^E = \mathbf{V}_n^E = 4\pi\boldsymbol{\alpha}\delta(\mathbf{r}-\mathbf{R}), \; \mathbf{T}_n^M = \mathbf{V}_n^M = 4\pi\boldsymbol{\beta}\delta(\mathbf{r}-\mathbf{R}),$$

for a nanoparticle at position $\mathbf{R}$ with electric (magnetic) polarizability tensors $\boldsymbol{\alpha}$ ($\boldsymbol{\beta}$). The approximation being made here is that the nanoparticle is a small object, and it is adequate to ignore higher multipoles. That is justified if a, a characteristic size of the particle, is $a \ll Z$.

CP free emergy

Then we are left with the following formula for the Casimir-Polder free energy between a polarizable nanoparticle and a conducting plate,

$$F_{np} = -2\pi \,\mathrm{Tr}\left(\boldsymbol{\alpha}\boldsymbol{\Gamma}_0\mathbf{T}_p\boldsymbol{\Gamma}_0 + \boldsymbol{\beta}\boldsymbol{\Phi}_0\mathbf{T}_p\boldsymbol{\Phi}_0\right).$$

Here $\mathbb{T}_p$ is the purely electric scattering operator for the conducting plate, which is immediately written in terms of the Green's operator Γ for a perfectly conducting plate,

$$\boldsymbol{\Gamma}_0\mathbf{T}_p\boldsymbol{\Gamma}_0 = \boldsymbol{\Gamma} - \boldsymbol{\Gamma}_0.$$

α polarization of nanoparticle

It is well-known that the Green's dyadic for a perfectly conducting plate lying in the $z = 0$ plane is for $z > 0$ given by the image construction

$$(\mathbf{\Gamma} - \mathbf{\Gamma}_0)(\mathbf{r}, \mathbf{r}') = -\mathbf{\Gamma}_0(\mathbf{r}, \mathbf{r}' - 2\hat{\mathbf{z}}z') \cdot (\mathbf{1} - 2\hat{\mathbf{z}}\hat{\mathbf{z}}),$$

where the free Green's dyadic is given above. Explicitly, for $\mathbf{R} = \mathbf{r} - \mathbf{r}'$,

$$\mathbf{\Gamma}_0(\mathbf{r}, \mathbf{r}') = -[\mathbf{1}u(|\zeta|R) - \hat{\mathbf{R}}\hat{\mathbf{R}}v(|\zeta|R)]\frac{e^{-|\zeta|R}}{4\pi R^3},$$

$$u(x) = 1 + x + x^2, \quad v(x) = 3 + 3x + x^2.$$

CP energy, $T \neq 0$

Let us first consider zero temperature. Then, if we ignore the frequency dependence of α, we integrate over imaginary frequency, and we immediately obtain the famous Casimir-Polder result

$$E^E_{np} = -\int_{-\infty}^{\infty} d\zeta \, \mathrm{tr}\, \boldsymbol{\alpha} \cdot (\boldsymbol{\Gamma} - \boldsymbol{\Gamma}_0)(\mathbf{R}, \mathbf{R}) = -\frac{\mathrm{tr}\, \boldsymbol{\alpha}}{8\pi Z^4}.$$

For nonzero T, we replace the integral by a sum,

$$\int_{-\infty}^{\infty} \frac{d\zeta}{2\pi} \to T \sum_{m=-\infty}^{\infty}, \quad \zeta \to \zeta_m = 2\pi m T.$$

Anisotropic Nanoparticle

If we assume the principal axis of the nanoparticle aligns with the direction normal to the plate,

$$\boldsymbol{\alpha} = \text{diag}(\alpha_\perp, \alpha_\perp, \alpha_z), \quad \gamma = \alpha_\perp/\alpha_z,$$

$$F^E_{np} = -\frac{3\alpha_z}{8\pi Z^4} f(\gamma, y),$$

$$f(\gamma, y) = \frac{y}{6}[(1+\gamma)(1 - y\partial_y) + \gamma y^2 \partial_y^2] \frac{1}{2} \coth \frac{y}{2}$$

where $y = 4\pi Z T$, where $Z =$ separation.

CP Entropy

The entropy is

$$S_{np}^{E} = -\frac{\partial}{\partial T} F_{np}^{E} = \frac{3\alpha_z}{2Z^3} \frac{\partial}{\partial y} f(\gamma, y),$$

so we define the scaled entropy by

$$s(\gamma, y) = \frac{\partial}{\partial y} f(\gamma, y).$$

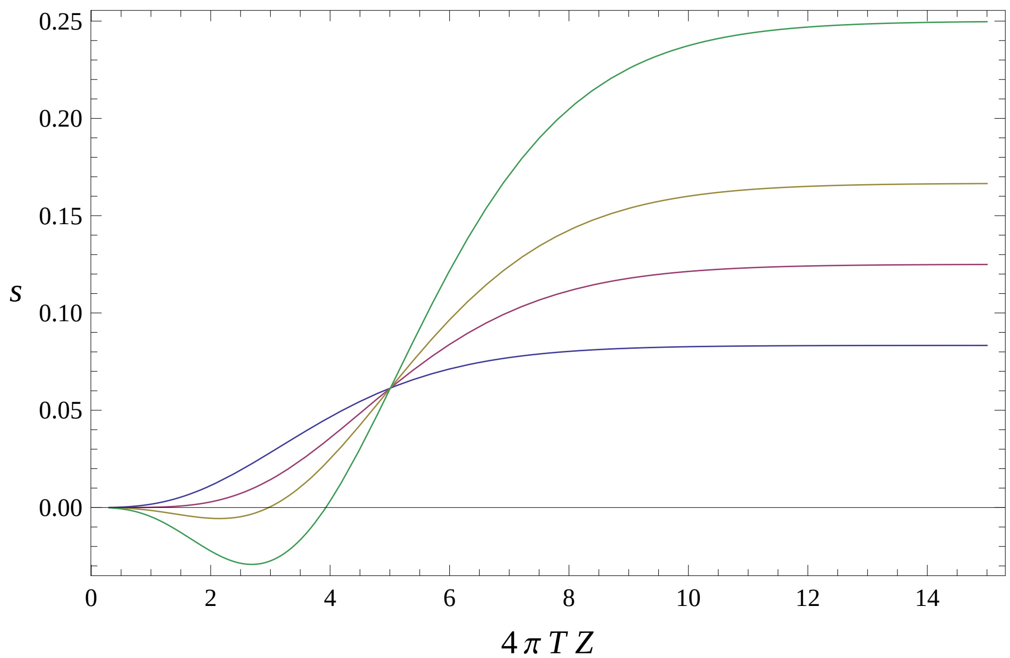
For small (large) y,

$$s(\gamma, y) \sim \frac{1}{540}(1-2\gamma)y^3 + O(y^5), \quad s(\gamma, y) \sim \frac{1}{12}(1+\gamma).$$

Negative entropy

The entropy vanishes at $T = 0$, and then starts off negative for small y when $\gamma > 1/2$. In particular, even for an isotropic, solely electrically polarizable, nanoparticle, where $\gamma = 1$, the entropy is negative for a certain region in y, as discovered by Bezerra et al. The behavior of the entropy with γ is illustrated in the following figure. For an isotropic nanoparticle, the negative entropy region occurs for $4\pi ZT < 2.97169$, or at temperature 300 K, for distances less than 2 μm.

Entropy atom-plate

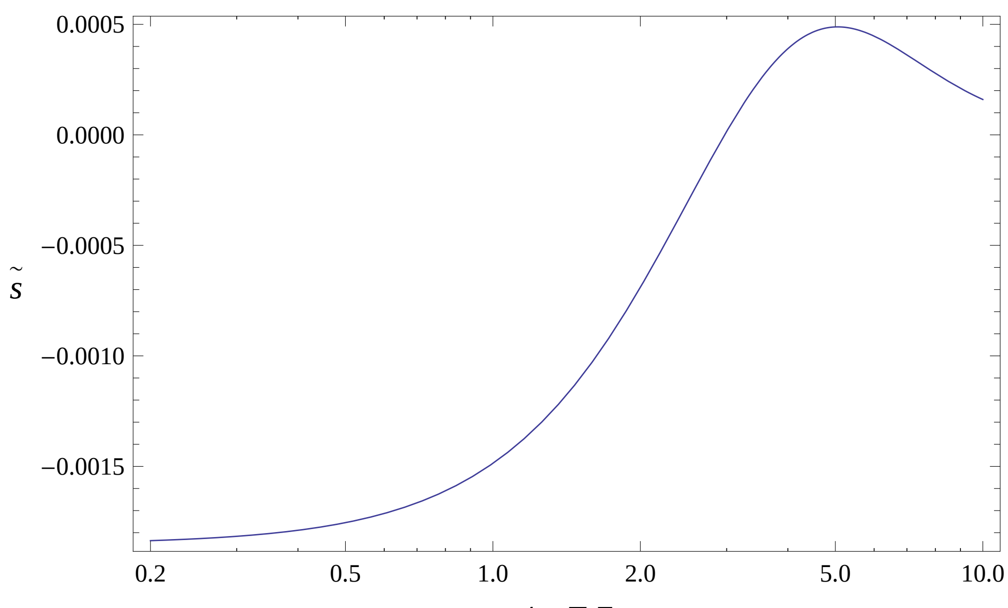


Scaled entropy s between a purely electrically polarizable nanoparticle and a conducting plate. Bottom to top for large ZT: $\gamma = 0$ (blue), $1/2$ (red), 1 (yellow), 2 (green).

Resecaled entropy

Most Casimir experiments are performed at room temperature. Therefore, it might be better to present the entropy in the form

$$S^E_{np} = \frac{3\alpha_z}{2}(4\pi T)^3 \tilde{s}(\gamma, y), \quad \tilde{s}(\gamma, y) = y^{-3} s(\gamma, y),$$



E and H polarizations of plate

To understand this phenomenon better, let us break up the polarization states of the conducting plate. For this purpose, it is convenient to use the $2+1$-dimensional breakup of the Green's dyadic. Following the formalism, we find that the free Green's dyadic has the form ($(d\mathbf{k}_\perp) = d^2k_\perp$)

$$\mathbf{\Gamma}_0(\mathbf{r}, \mathbf{r}') = \int \frac{(d\mathbf{k}_\perp)}{(2\pi)^2} e^{i\mathbf{k}_\perp\cdot(\mathbf{r}-\mathbf{r}')_\perp} (\mathsf{E}+\mathsf{H})(z, z') \frac{1}{2\kappa} e^{-\kappa|z-z'|},$$

which readily leads to the representation for the free energy for the nanoparticle-plate system

Free energy particle/plate

$$F^E = 2\pi T \sum_{m=-\infty}^{\infty} \int \frac{(d\mathbf{k}_\perp)}{(2\pi)^2} \mathrm{tr}[\boldsymbol{\alpha}\cdot(\mathsf{E}-\mathsf{H})(Z,Z)] \frac{1}{2\kappa} e^{-2\kappa Z},$$

where $\kappa^2 = k_\perp^2 + \zeta_m^2$. Here the TE and TM polarization tensors are, after averaging over the directions of $\mathbf{k}_\perp$,

$$\mathsf{E} = -\frac{\zeta^2}{2}\mathbf{1}_\perp, \quad \mathsf{H} = \frac{\kappa^2}{2}\mathbf{1}_\perp + (\kappa^2 - \zeta_m^2)\hat{\mathbf{z}}\hat{\mathbf{z}}.$$

TE contribution to F

Performing the elementary integrals and sums, we get for the TE contribution to the free energy

$$F_E^E = -\frac{3\alpha_z}{8\pi Z^4} f_E(\gamma, y), \quad f_E(\gamma, y) = \gamma \frac{y^3}{12} \partial_y^2 \left(\frac{1}{2} \coth \frac{y}{2} \right)$$

$$S_E^E = -\frac{\partial}{\partial T} F_E^E = \frac{3\alpha_z}{2Z^3} s_E(\gamma, y), \quad s_E(\gamma, y) = \frac{\partial}{\partial y} f_E(\gamma, y)$$

Large and small $y = 4\pi ZT$

For large y, s_E goes to zero exponentially,

$$s_E(\gamma, y) \sim -\frac{\gamma}{12} y^2 (y-3) e^{-y}, \quad y \gg 1,$$

while for small y,

$$s_E(\gamma, y) \sim -\gamma \frac{y^3}{360} + O(y^5), \quad y \ll 1.$$

The transverse electric contribution to the entropy, s_E, is always negative.

TM polarization

On the other hand, $s_H = s - s_E$ is positive for large y,

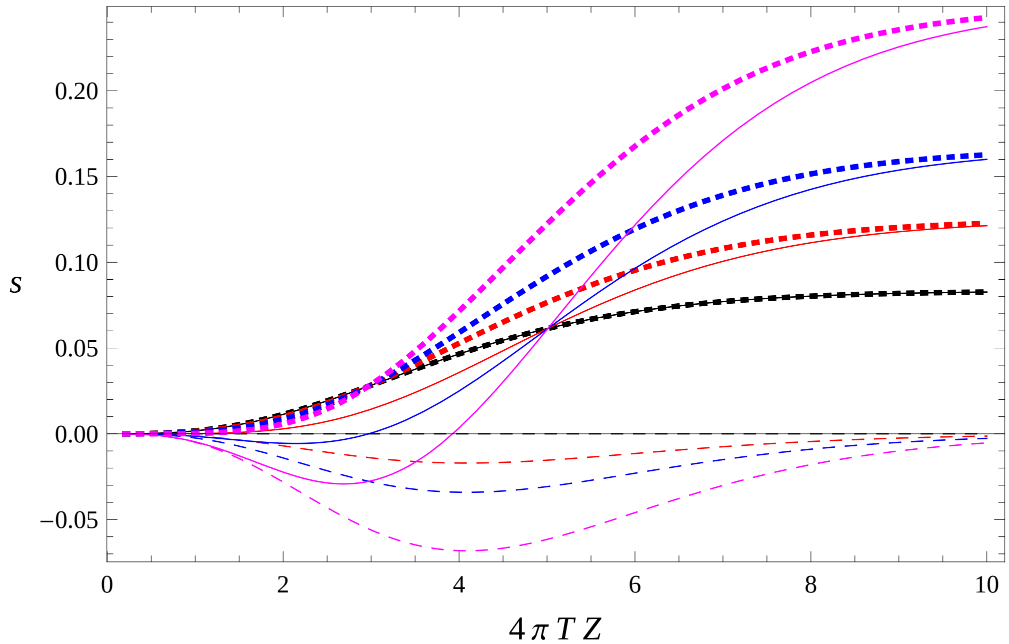
$$s_H \sim \frac{1+\gamma}{12}, \quad y \gg 1,$$

but can change sign for small y,

$$s_H(\gamma, y) \sim \frac{y^3}{540}\left(1 - \frac{1}{2}\gamma\right), \quad y \ll 1.$$

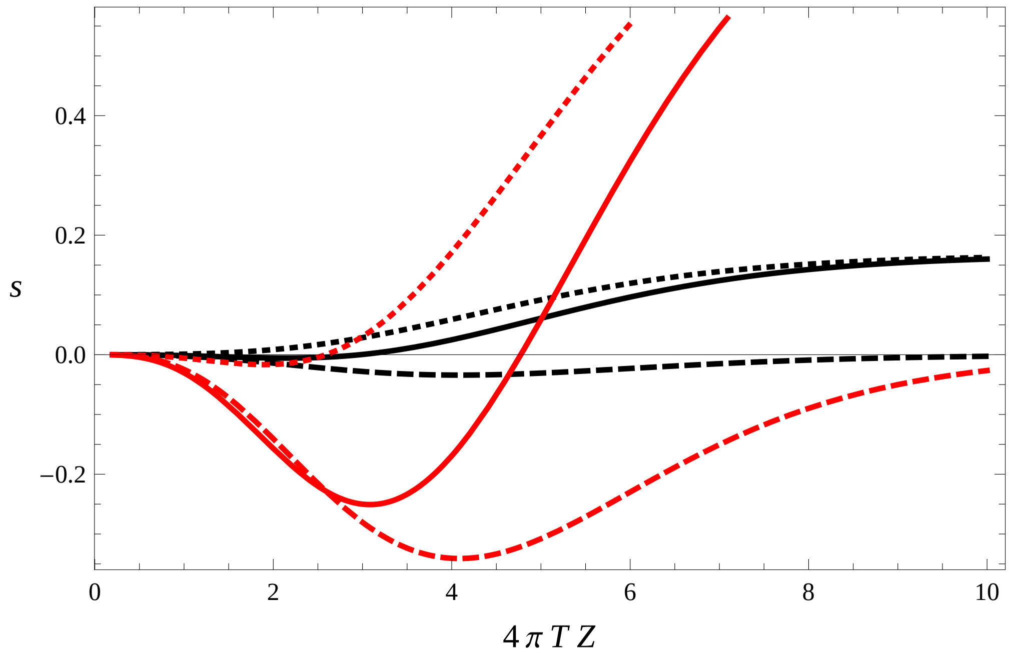
So s_H can change sign for $\gamma > 2$; the total entropy s can change sign for $\gamma > 1/2$. These features are illustrated in the following figure.

Plate-Nanoparticle Entropy



The solid curves are the total entropy, the short-dashed curves are for the TM plate contribution, and the long-dashed curves are for TE. Black: $\gamma = 0$, red: $\gamma = 1/2$, blue: $\gamma = 1$, magenta: $\gamma = 2$.

Entropy of purely electrical particle



This illustrates that even for a solely electrically polarizable nanoparticle S_H can turn negative for $\gamma > 2$. black: $\gamma = 1$, red: $\gamma = 10$. Again: s: solid curves, s_E: long-dashed curves, and s_H: short-dashed curves.

Drude vs. plasma model

Note that there is no difference between a perfectly conducting plate and one represented by the ideal Drude model, which differs from the former only by the exclusion of the TE $m = 0$ mode. This is because this term does not contribute to F_E^E or to S_E^E.

β polarization of nanoparticle

Now we turn to the magnetic polarizability of the nanoparticle, All we need is the scattering operator for the conducting plate,

$$\mathbf{T}_p(\mathbf{r},\mathbf{r}') = \int \frac{(d\mathbf{k}_\perp)}{(2\pi)^2} e^{i\mathbf{k}_\perp\cdot(\mathbf{r}-\mathbf{r}')_\perp} \frac{1}{\zeta^2}(\mathsf{E}-\mathsf{H})(z,z') \cdot\delta(z) e^{-\kappa|z'|}.$$

Green's dyadic

Then the Green's dyadic appearing there can be written in terms of the polarization operators for the plate as

$$\boldsymbol{\Phi}_0 \cdot \mathbf{T}_p \cdot \boldsymbol{\Phi}_0(Z, Z) = \int dz'\, dz'' \int \frac{(d\mathbf{k}_\perp)}{(2\pi)^2}$$

$$\left(-\frac{1}{\zeta}\boldsymbol{\nabla} \times (\mathsf{E} + \mathsf{H})(Z, z')\frac{1}{2\kappa}e^{-\kappa|Z-z'|}\right)\frac{1}{\zeta^2}(\mathsf{E} - \mathsf{H})(z', z'')$$

$$\left(-\frac{1}{\zeta^2}\boldsymbol{\nabla}'' \times \boldsymbol{\nabla}'' \times -\mathbf{1}\right) e^{-\kappa|z''|}\left(-\frac{1}{\zeta}\boldsymbol{\nabla}'' \times (\mathsf{E} + \mathsf{H})(z'', Z\right.$$

$$\left. \cdot \frac{1}{2\kappa}e^{-\kappa|z''-Z|}\right).$$

Simplification

The intermediate wave operator here annihilates the following Green's dyadic except on the plate:

$$\left(-\frac{1}{\zeta^2}\boldsymbol{\nabla}'' \times \boldsymbol{\nabla}'' \times -\mathbf{1}\right) e^{-\kappa|z''|} \cdot \boldsymbol{\nabla}'' \times (\mathsf{E}+\mathsf{H})$$

$$= \left(\frac{1}{\zeta^2}\nabla''^2 - 1\right) e^{-\kappa|z''|}\boldsymbol{\nabla}'' \times (\mathsf{E}+\mathsf{H})$$

$$= -\frac{2\kappa}{\zeta^2}\delta(z'')\boldsymbol{\nabla}'' \times (\mathsf{E}+\mathsf{H}).$$

Properties of Polarization Operators

Now we integrate by parts and use the identities

$$\begin{aligned}\boldsymbol{\nabla}' \times (\mathsf{E}-\mathsf{H})(z',z'') \times \boldsymbol{\nabla}'' &= -\zeta^2(\mathsf{E}-\mathsf{H}),\\ \mathsf{E}(z,z')\cdot\mathsf{E}(z',z'') &= -\zeta^2\mathsf{E}(z,z''),\\ \mathsf{H}(z,z')\cdot\mathsf{H}(z',z'') &= -\zeta^2\mathsf{H}(z,z''),\\ \mathsf{E}(z,z')\cdot\mathsf{H}(z',z'') &= 0.\end{aligned}$$

Magnetic Green's dyadic

In this way we find the magnetic Green's dyadic appearing in the formula for the magnetic part of the Casimir-Polder energy to be

$$\mathbf{\Phi}_0\mathbf{T}_p\mathbf{\Phi}_0(Z,Z) = -\int\frac{(d\mathbf{k}_\perp)}{(2\pi)^2}(\mathsf{E}-\mathsf{H})(Z,Z)e^{-2\kappa Z},$$

which is just negative of the corresponding expression for the electric Green's dyadic.

Total Free Energy

Thus the expression for the magnetic polarizability contribution is obtained from the free energy for the electric polarizability by the replacement $\boldsymbol{\alpha} \to -\boldsymbol{\beta}$, and the total free energy for the nanoparticle-plate system is given by

$$F = 2\pi T \sum_{m=-\infty}^{\infty} \int \frac{(d\mathbf{k}_\perp)}{(2\pi)^2} \operatorname{tr}[(\boldsymbol{\alpha} - \boldsymbol{\beta}) \cdot (\mathsf{E} - \mathsf{H})(Z, Z)] \cdot \frac{1}{2\kappa} e^{-2\kappa Z}.$$

Electric/Magnetic Equality

This simple relation between the electric and magnetic polarizability contributions was noted earlier. In particular, for the interesting case of a conducting sphere, the previous results apply, except multiplied by a factor of 3/2. In that case, the limiting value of the entropy is

$$S(T) \sim -\frac{4}{15}(\pi a T)^3, \quad 4\pi Z T \ll 1.$$

CP interaction of 2 nanoparticles

Let us now consider two nanoparticles, one located at the origin and one at $\mathbf{R} = (0, 0, Z)$. Let the nanoparticles have both static electric and magnetic polarizabilities $\boldsymbol{\alpha}_i$, $\boldsymbol{\beta}_i$, $i = 1, 2$. We will again suppose the nanoparticles to be anisotropic, but, for simplicity, having their principal axes aligned with the direction connecting the two nanoparticles:

$$\boldsymbol{\alpha}_i = \text{diag}(\alpha^i_\perp, \alpha^i_\perp, \alpha^i_z), \quad \boldsymbol{\beta}_i = \text{diag}(\beta^i_\perp, \beta^i_\perp, \beta^i_z).$$

The methodology is very similar to that explained in the particle/plate discussion.

Electric polarizability

We start with the interaction between two electrically polarizable nanoparticles. The free energy is

$$F^{EE} = -\frac{T}{2} \sum_{m=-\infty}^{\infty} \mathrm{tr}[4\pi \boldsymbol{\alpha}_1 \cdot \boldsymbol{\Gamma}_0(\mathbf{R}) \cdot 4\pi \boldsymbol{\alpha}_2 \cdot \boldsymbol{\Gamma}_0(\mathbf{R})],$$

where the free Green's dyadic is given above. A simple calculation yields ($y = 4\pi ZT$)

$$F^{EE} = -\frac{23}{4\pi Z^7} \alpha_z^1 \alpha_z^2 f(\gamma, y).$$

Scaled free energy

where

$$f(\gamma, y) = \frac{y}{23}\left[4\left(1 - y\partial_y + \frac{1}{4}y^2\partial_y^2\right)\right.$$
$$\left. + 2\gamma\left(1 - y\partial_y + \frac{3}{4}y^2\partial_y^2 - \frac{1}{4}y^3\partial_y^3 + \frac{1}{16}y^4\partial_y^4\right)\right]$$

Here $\gamma = \gamma_1\gamma_2$, where $\gamma_i = \alpha_\perp^i/\alpha_z^i$.

CP Entropy

The entropy is

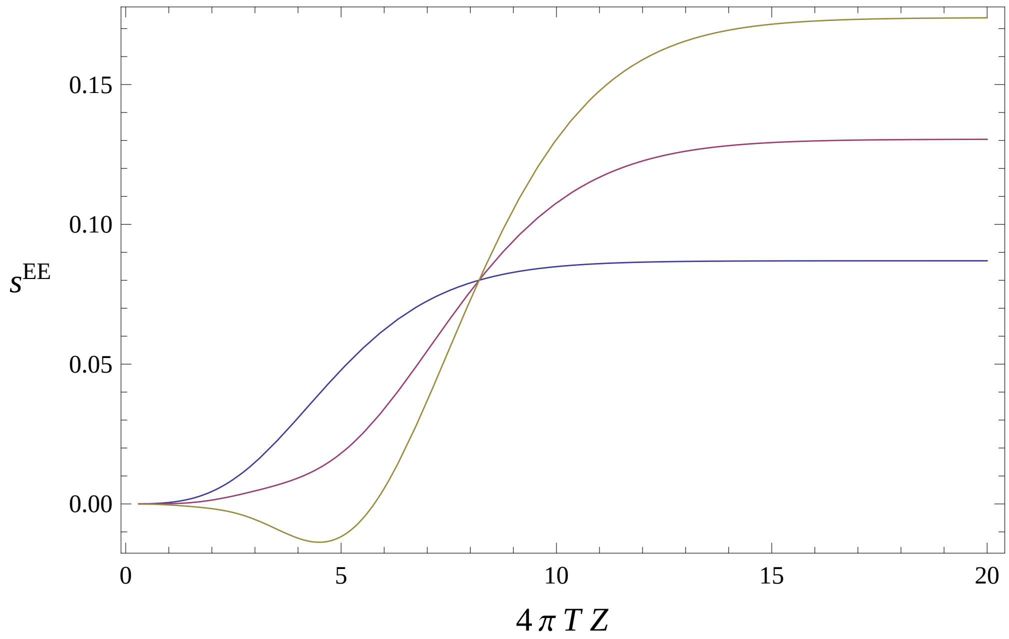
$$S^{EE} = \frac{23\alpha_z^1\alpha_z^2}{Z^6} s^{EE}(\gamma, y), \quad s^{EE}(\gamma, y) = \frac{\partial}{\partial y} f(\gamma, y).$$

The asymptotic limits are

$$s^{EE}(\gamma, y) \sim \frac{2+\gamma}{23}, \quad y \gg 1,$$
$$s^{EE}(\gamma, y) \sim \frac{1}{2070}(1-\gamma)y^3, \quad y \ll 1,$$

so even in the pure electric case there is a region of negative entropy for $\gamma > 1$, illustrated below.

Transverse electric polarizabilities



The entropy $s^{EE}(\gamma, y)$ for two anisotropic purely electrically polarizable nanoparticles with separation Z and temperature T. When $\gamma = \gamma_1\gamma_2 > 1$ the entropy can be negative. Blue: $\gamma = 0$, red: 1, yellow: 2.

EM cross term

For the “interference” term between the magnetic polarization of one nanoparticle and the electric polarization of the other, we compute the free energy from the third term in the master equation

$$F^{EM} = -\frac{1}{2}\mathrm{tr}[\mathbf{\Phi}_0 \cdot 4\pi\boldsymbol{\alpha}_1 \cdot \mathbf{\Phi}_0 \cdot 4\pi\boldsymbol{\beta}_2] + (1 \leftrightarrow 2).$$

This is easily worked out using the following simple form of the Φ_0 operator

$$\mathbf{\Phi}_0(\mathbf{R}) = -\frac{\zeta_m}{4\pi Z^3}\mathbf{R} \times (1 + \zeta_m Z)e^{-|\zeta_m|Z}, \quad Z = |\mathbf{R}|.$$

Free energy

The result for the free energy is

$$F^{EM} = \frac{7}{4\pi Z^7}(\alpha_\perp^1 \beta_\perp^2 + \beta_\perp^1 \alpha_\perp^2) g(y),$$

which is normalized to the familiar zero temperature result, where

$$g(y) = \frac{y}{14}\left(y^2\partial_y^2 - y^3\partial_y^3 + \frac{1}{4}y^4\partial_y^4\right)\frac{1}{2}\coth\frac{y}{2}.$$

Entropy

The entropy is

$$S^{EM} = -\frac{7}{Z^6}(\alpha^1_\perp \beta^2_\perp + \beta^1_\perp \alpha^2_\perp) s^{EM}, \qquad s^{EM}(y) = \frac{\partial g(y)}{\partial y}.$$

This is always negative, vanishes exponentially fast for large y, and also vanishes rapidly for small y,

$$s^{EM} \sim -\frac{y^5}{7056}.$$

General results

We can present the total entropy for two nanoparticles having both electric and magnetic polarizabilities as follows,

$$S = \frac{1}{Z^6}\Big[23\alpha_z^1\alpha_z^2 s^{EE}(\gamma_\alpha^1\gamma_\alpha^2, y) + 23\beta_z^1\beta_z^2 s^{EE}(\gamma_\beta^1\gamma_\beta^2, y)$$

$$- 7(\alpha_z^1\beta_z^2\gamma_\alpha^1\gamma_\beta^2 + \beta_z^1\alpha_z^2\gamma_\beta^1\gamma_\alpha^2)s^{EM}(y)\Big],$$

where s^{EE} and s^{EM} are given by above.

Small $y = 4\pi ZT$

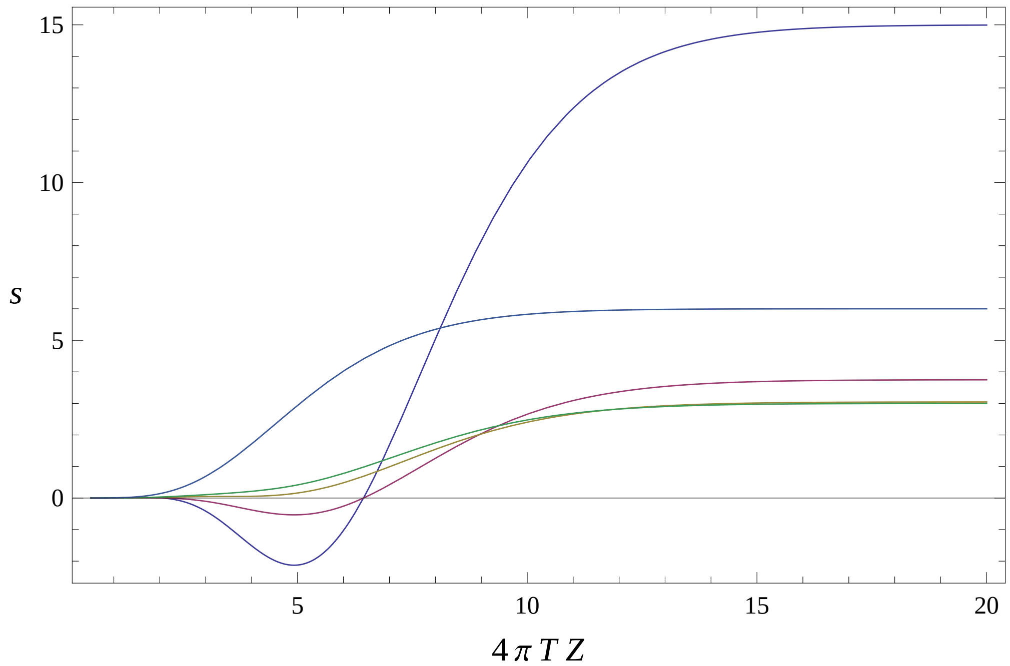
For small y, the leading behavior of the entropy is

$$S = \frac{y^3}{90R^6}[\alpha_z^1\alpha_z^2(1-\gamma_\alpha^1\gamma_\alpha^2) + \beta_z^1\beta_z^2(1-\gamma_\beta^1\gamma_\beta^2)]$$
$$+ \frac{y^5}{5040R^6}[\alpha_z^1\alpha_z^2(4+7\gamma_\alpha^1\gamma_\alpha^2) + \beta_z^1\beta_z^2(4+7\gamma_\beta^1\gamma_\beta^2)$$
$$+ 5(\alpha_z^1\beta_z^2\gamma_\alpha^1\gamma_\beta^2 + \beta_z^1\alpha_z^2\gamma_\beta^1\gamma_\alpha^2) + O(y^7).$$

Graphs

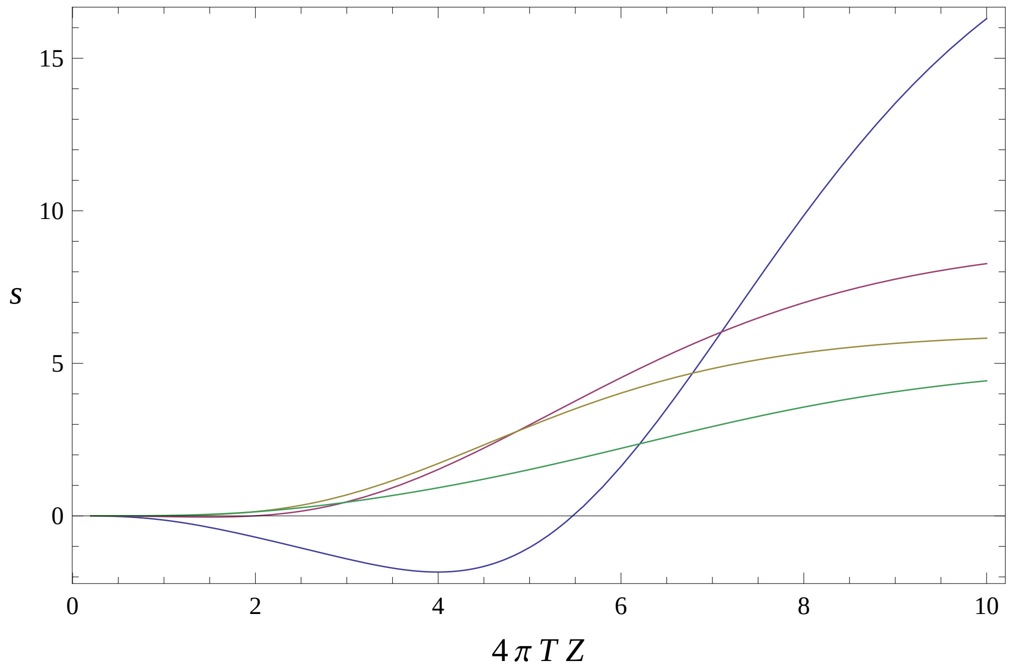
In the following six figures we present graphs of the entropy for the case of identical nanoparticles, for simplicity, $\alpha_z^1 = \alpha_z^2$, $\beta_z^1 = \beta_z^2$, $\gamma_\alpha^1 = \gamma_\alpha^2$, $\gamma_\beta^1 = \gamma_\beta^2$. In the first figure we show the entropy for isotropic nanoparticles with different ratios of magnetic to electric polarizabilities; negative entropy appears when the ratio is smaller than about $-1/8$. This is a nonperturbative effect. Thus, perfectly conducting spheres, $\beta/\alpha = -1/2$, exhibit $S < 0$.

Entropy of identical nanoparticles



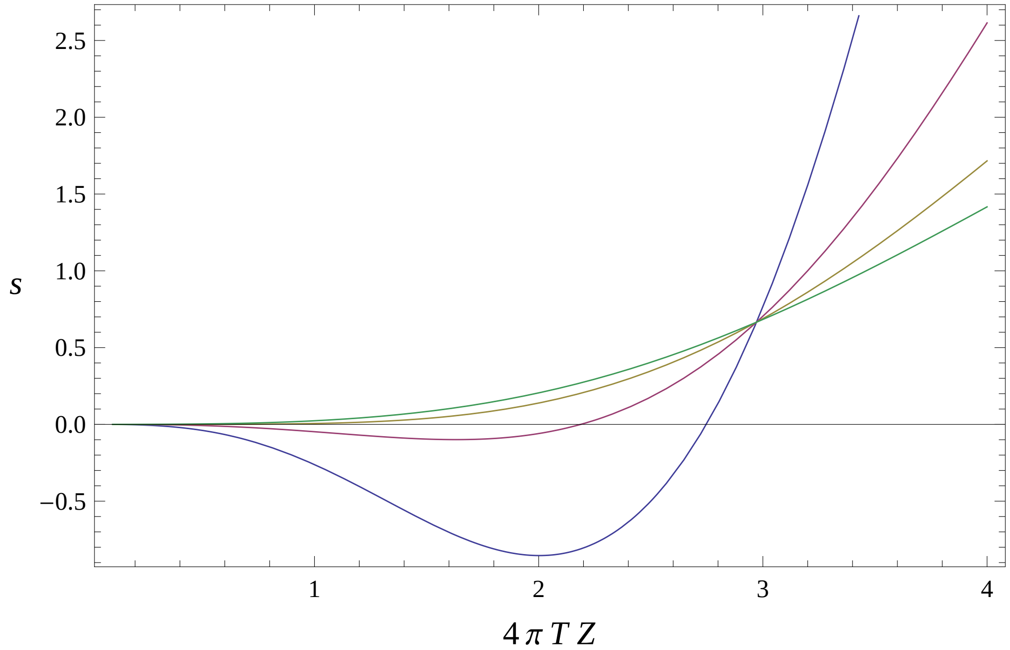
Entropy of two identical isotropic nanoparticles ($\gamma_\alpha = \gamma_\beta = 1$) for different values of $r = \beta/\alpha$. Purple: $r = 1$, green: 0 , yellow: $-1/8$, red: $-1/2$ (red), -2 (blue).

Anisotropic electric polarizabilities



Here the identical nanoparticles have equal values of $\alpha_z = \beta_z$, and $\gamma_\beta = 1$, but different values of the electric anisotropy. $\gamma_\alpha = 0$ (green), 1 (yellow), 2 (red), 4 (blue), respectively.

Equal anisotropies

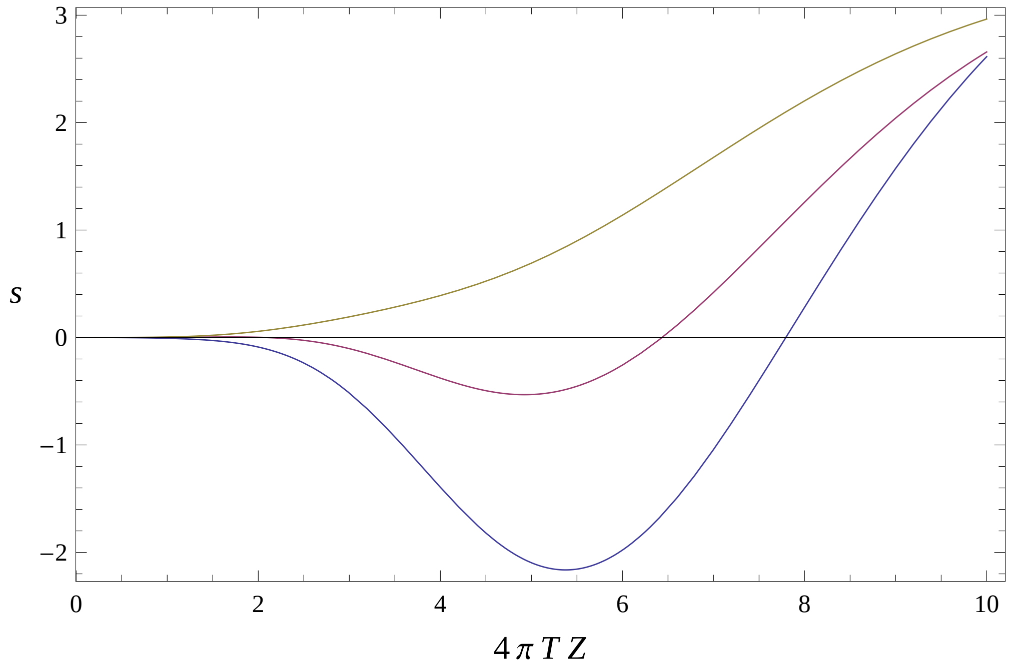


Here the identical nanoparticles have equal electric and magnetic polarizabilities, and equal anisotropies. $\gamma = 0$ (green), 1 (yellow), 2 (red), 4 (blue), respectively.

Perfectly conducting nanoparticles

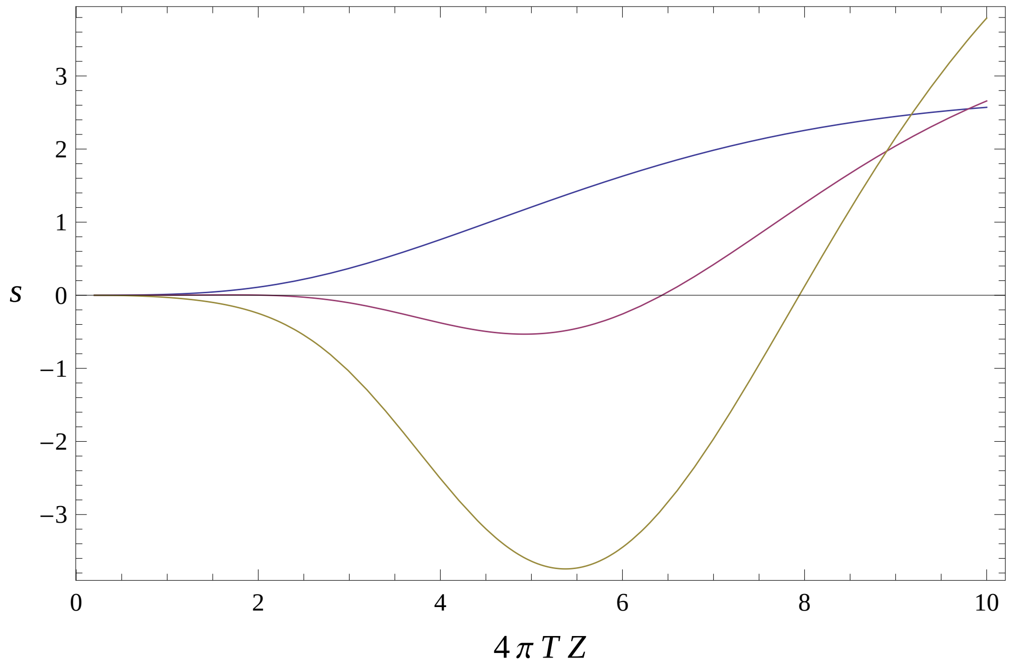
The case of a conducting sphere has $\beta = -\alpha/2$. We examine this situation in the following figure, for different magnetic anisotropies, and in next figure, for different electric anisotropies. In this case the leading term in S vanishes at $\gamma = 1$, so the appearance of negative entropy for $\gamma \leq 1$ is non-perturbative. In fact, the boundary values for the two cases are $\gamma_\beta = 0.5436$ and $\gamma_\alpha = 0.7427$, respectively. For the latter case, this is illustrated in the third figure.

Identical conducting spheres



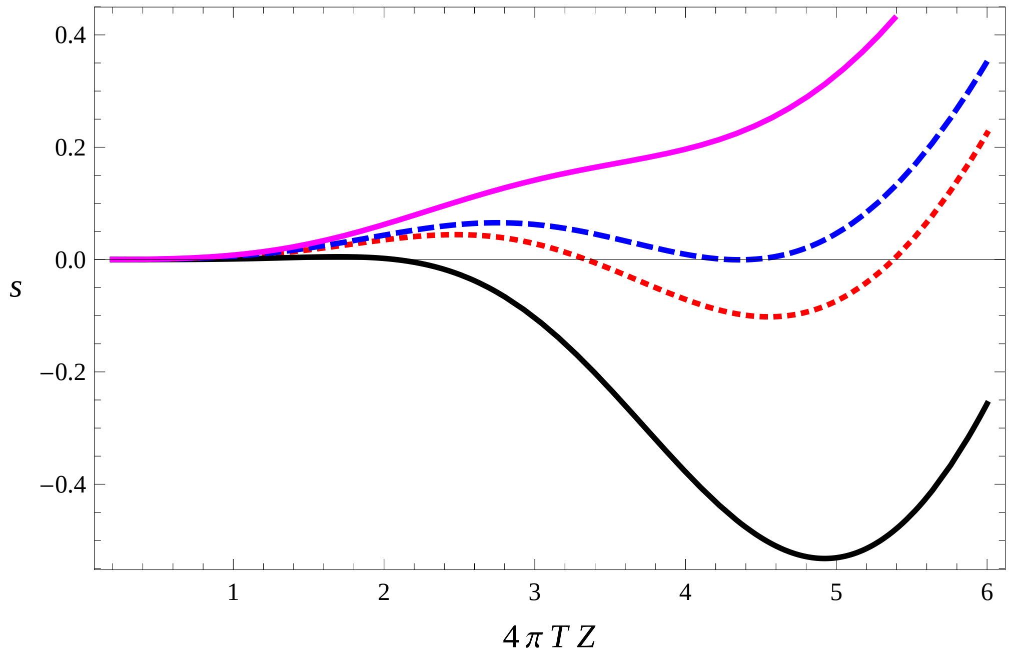
The case of two identical conducting spheres where $\alpha_z = -2\beta_z$, with electrical isotropy, but magnetic anisotropy $\gamma_\beta = 0$ (yellow), 1 (red), 2 (blue), reading from top to bottom.

Conducting, electrically anisotropic



The case of two identical conducting nanoparticles where $\alpha_z = -2\beta_z$, with magnetic isotropy, but electric anisotropy $\gamma_\alpha = 0$ (blue), 1 (red), 2 (yellow), reading from top to bottom in the middle.

Nonperturbative negative entropy

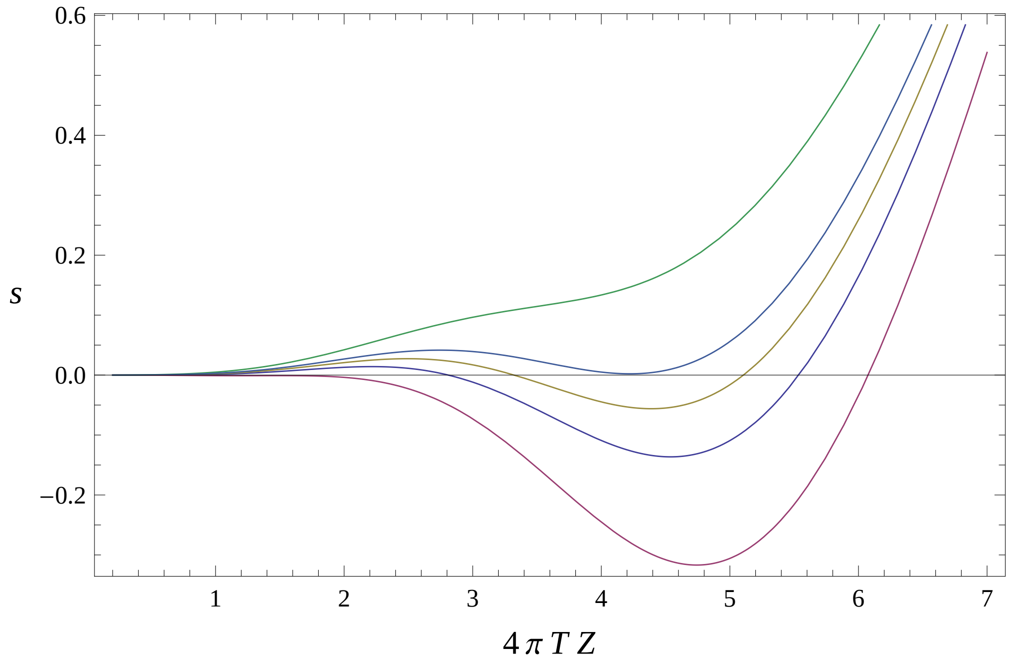


Two identical nanoparticles with $\beta_z = -\alpha_z/2$, appropriate for a conducting sphere, isotropic magnetically, $\gamma_\alpha = 0.6$ (magenta), 0.743 (dashed blue), 0.8 (short dashed red), 1 (black).

Conducting and Drude nanoparticle

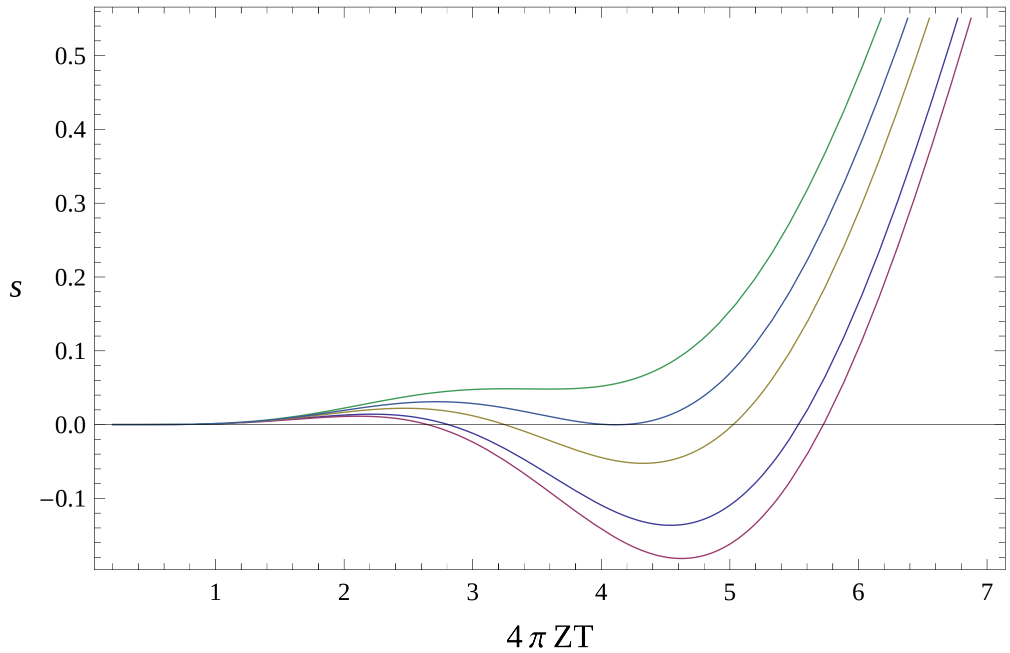
An interesting case is the interaction of a perfectly conducting nanoparticle with a Drude nanoparticle, by which we mean that the latter has vanishing magnetic polarizability. In the next figure we consider the electric anisotropies to be the same, while in the following figure we show how the entropy changes as we vary the anisotropy of the magnetic polarizability of the perfectly conducting sphere. For isotropic spheres there is always a region of negative entropy.

Conducting/Drude nanopaticles



Interaction entropy between a perfectly conducting nanoparticle, $\beta_1 = -\frac{1}{2}\alpha_1$, and a Drude nanoparticle with $\alpha_2 = \alpha_1$, $\beta_2 = 0$. $\gamma_\beta = 0$, $\gamma_{\alpha 1} = \gamma_{\alpha 2}$. Green: $\gamma_\alpha = 0.8$, purple: 0.91, yellow: 0.95, blue: 1.0, and red: 1.1.

Conducting/Drude spheres, $=\alpha$'s



Interaction entropy between a perfectly conducting nanoparticle, $\beta_1 = -\frac{1}{2}\alpha_1$, and a Drude nanoparticle with $\alpha_2 = \alpha_1$, $\beta_2 = 0$. $\gamma_\alpha = 0$. Green: $\gamma_{\beta 1} = 0.5$, purple: 0.66, yellow: 0.8, blue: 1, red: 1.1.

Conclusions

In this talk we have studied purely geometrical aspects of the entropy that arise from the Casimir-Polder interaction, either between a polarizable nanoparticle and a conducting plate, or between two polarizable nanoparticles. We consider the simplified long distance regime where we may regard both the electric and magnetic polarizabilities of the nanoparticles as constant in frequency. Thus, throughout we are assuming that the separations $Z \gg a$.

Conclusions (cont.)

It has been known for some time that negative entropy can occur between a purely electrically polarizable isotropic nanoparticle and a perfectly conducting plate. Here we consider both electric and magnetic polarization for both the nanoparticle and the plate. Negative entropy frequently arises, but requires interplay between electric and magnetic polarizations, or anisotropy, in that the polarizability of the nanoparticles must be different in different directions.

Perturbative/nonperturbative effect

Interestingly, although in some cases the negative entropy is already contained in the leading low-temperature expansion of the entropy, in other cases negative entropy is a nonperturbative effect, not contained in the leading behavior of the coefficients of the low temperature expansion. What we observe here mirrors what has been found in, for example, calculations of the entropy between a finite sphere and a plate.

Summary

We summarize our findings in the following Table, which, we again emphasize, refer to the dipole approximation, appropriate in the long-distance regime, $Z \gg a$. Surprisingly, perhaps, negative entropy is a nearly ubiquitous phenomenon: Negative entropy typically occurs when a polarizable nanoparticle is close to another such particle or to a conducting plate. This is not a thermodynamic problem because we are considering only the interaction entropy, not the total entropy.

Summary Table

Two nanoparticle or particle/plate	Negative entropy?
E/E	$S < 0$ occurs for $\gamma_\alpha > 1$
E/M	$S < 0$ always
PC/PC	$S < 0$ for $\gamma_\alpha > 0.74$ or $\gamma_\beta > 0.54$
PC/D	$S < 0$ for $\gamma_\alpha > 0.91$ or $\gamma_\beta > 0.66$
E/TE plate	$S < 0$ always
E/TM plate	$S < 0$ for $\gamma_\alpha > 2$
E/PC or D plate	$S < 0$ for $\gamma_\alpha > 1/2$