The Casimir Effect and Thermodynamic Instability

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ABSTRACT

One loop field theory calculations of free energies quite often yield violations of the stability conditions usually associated with the thermodynamic second law. Perhaps the best known example involves the equation of state of black holes. Here, it is pointed out that the Casimir force between two parallel conducting plates also violates a thermodynamic stability condition normally associated with the second law of thermodynamics.

1. Introduction

A property shared by many one loop quantum statistical thermodynamic computations is that a thermodynamic second law instability appears in the final answer. Perhaps the most commonly discussed example of this phenomena occurs in black hole statistical thermodynamics [1,2]. The entropy $S$ of a black hole having mass $M$ is given by

$$ S = 4\pi k_B \left( \frac{GM^2}{\hbar c} \right), \quad (1.1) $$

where $G$ is Newton’s gravitational coupling strength. The black hole temperature, defined as $T = c^2 (\partial M/\partial S)$, is then determined by

$$ M = \left( \frac{\hbar c^3}{8\pi G k_B T} \right). \quad (1.2) $$

The black hole heat capacity $C = c^2 (\partial M/\partial T)$ is thereby negative,

$$ C = \frac{k_B}{\frac{\hbar c^5}{8\pi G (k_B T)^2}} = -\left( \frac{1}{8\pi} \right) \left( \frac{\hbar c}{k_B T \Lambda} \right)^2 < 0, \quad (1.3) $$

which violates the second law of thermodynamics. In Eq.(1.3), $\Lambda$ is the Planck length.

That a one loop quantum gravity calculation, i.e. the gravitational Casimir effect, produces a theoretical violation of the thermodynamic second law is (perhaps) not very surprising. Even at the Newtonian theoretical level, the long range gravitational attraction
upsets the usual second law convexity conditions otherwise present in the thermodynamic limit of infinite size.

Our purpose is to show the perhaps more surprising result that the electrodynamic Casimir effect can also produce a second law violation, which should be present in laboratory experiments. To see what is involved, suppose that a material is located inside a box of volume \( V \). The free energy obeys the thermodynamic law

\[
dF = -SdT - PdV. \tag{1.4}
\]

If the box is a cylinder cavity with a cross sectional area \( A \), and a piston height \( z \), so that

\[
V = Az, \quad F = Af, \quad S = As, \tag{1.5}
\]

then the free energy per unit area obeys

\[
df = -sdT - Pdz, \tag{1.6}
\]

The second law of thermodynamics dictates that the isothermal compressibility

\[
K_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{1}{z}\right)\left(\frac{\partial z}{\partial P}\right)_T, \tag{1.6}
\]

obeys the inequality

\[
K_T \geq 0 \quad \text{(second law).} \tag{1.7}
\]

It is this above positive compressibility implication of the second law of thermodynamics that is violated by the vacuum in the conventional quantum electrodynamic Casimir effect.

## 2. Statistical Thermodynamics of the Casimir Effect

Consider two thick parallel conducting plates separated by a distance \( z \) with the “vacuum” material between the plates. Let \( f(z, T) \) be the free energy per unit area of this vacuum. The ground state energy per unit area of this vacuum is given by [3-5]

\[
\epsilon(z) = \lim_{T \to 0} f(z, T) = -\left(\frac{\pi^2}{720}\right)\left(\frac{\hbar c}{z^3}\right), \tag{2.1}
\]

yielding the pressure

\[
P_0 = \lim_{T \to 0} P(z, T) = -\left(\frac{\pi^2}{240}\right)\left(\frac{\hbar c}{z^4}\right). \tag{2.2}
\]

The zero temperature compressibility then reads

\[
K_0 = \lim_{T \to 0} K_T = -\left(\frac{60}{\pi^2}\right)\left(\frac{z^4}{\hbar c}\right) < 0. \tag{2.3}
\]

The negative compressibility \((K_0 < 0)\) in Eq.(2.3) violates the second law of thermodynamics, as written in Eq.(1.7).
3. Stability and High Frequency Driving Forces

If in addition to the Casimir effect one applies a voltage source $U$ across the plates, then the total free energy per unit area obeys

$$df_{tot} = -sdT - Pdz - \sigma dU,$$

(3.1)

where $\sigma$ represents that charge per unit area on the capacitor plates. The total free energy per unit area (in Gaussian units) for parallel plates with capacitance $C(z) = \{A/(4\pi z)\}$ obeys

$$f_{tot}(T, z, U) = f(T, z) - \left(\frac{U^2}{8\pi z}\right).$$

(3.2)

The Coulomb attraction last term on the right hand side of Eq. (3.3) only serves to enhance the thermodynamic second law violation in the compressibility of the space between the plates. In fact, even if the Coulomb force dominates the Casimir force one appears to still have a second law violation merely from Coulomb law.

Employing an experimental viewpoint, the situation becomes stable if the voltage has a high frequency AC as well as a DC component \[6\],

$$U = u + \sqrt{2}u_\omega \cos(\omega t).$$

(3.3)

After averaging over the high frequency force components, the effective energy per unit area ($T \rightarrow 0$) becomes

$$\bar{\epsilon}(z) = -\left(\frac{\pi^2}{720}\right)\left(\frac{hc}{z^3}\right) - \left(\frac{u^2 + u_\omega^2}{8\pi z}\right) + \left(\frac{K(\omega, u, u_\omega)}{z^4}\right),$$

(3.4)

where

$$K(\omega, u, u_\omega) = \left(\frac{1}{512\pi^2}\right)\left(\frac{u_\omega^4 + 8u^2u_\omega^2}{\mu\omega^2}\right).$$

(3.5)

and $\mu$ represents the mass per unit area of the vibrating capacitor plate.

Thermodynamic “stability” can be achieved at the equilibrium distance $z = Z$ which minimizes the energy $\bar{\epsilon}(z)$. This equilibrium does correspond to a positive compressibility $\bar{\epsilon}''(Z) > 0$. However, it requires continual total entropy production to maintain such vibrating plate “equilibrium” stability. This is not the normal sort of thing (say minimum energy at fixed entropy) thought to represent the equilibrium thermodynamic second law. However, such a high frequency technique might be useful experimentally.

4. Conclusions

The notion of negative compressibility matter is as old as the van der Waals approximation to the equations of state of a material [7]. It has always been stated that such equations of state require supplementary conditions such as equal area constructions and so forth (see for example Ref. 7 pp 257-62). Furthermore, the second thermodynamic law has been thought to put a complete and total veto on observing the totally unstable
part of the van der Waals curve; i.e. $K_T < 0$ exists formally in the approximation, but is strictly forbidden from observation.

So now we have a paradox, and perhaps an interesting energy source. For the Casimir force, and even for Coulomb law, the regime $K_T < 0$ may be asserted to be real. A closer study as to whether or not one can use such observable regimes to extract work in a cycle from an isothermal environment is underway.

References

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