On the Casimir entropy between ‘perfect crystals’

C. HENKEL* and F. INTRA VÀIA§

Institut für Physik und Astronomie, Universität Potsdam,
Karl-Liebknecht-Str. 24/25, 14476 Potsdam, Germany
*Email: henkel@uni-potsdam.de

We give a re-interpretation of an ‘entropy defect’ in the electromagnetic Casimir effect. The electron gas in a perfect crystal is an electromagnetically disordered system whose entropy contains a finite Casimir-like contribution. The Nernst theorem (third law of thermodynamics) is not applicable.

Keywords: Temperature; entropy; dissipation; overdamped mode.

1. Introduction

It is well known that fluctuation interactions at nonzero temperature are entropic in character, a prominent example being the critical Casimir effect in liquid mixtures close to a continuous phase transition (see Ref.1 for an overview). The electromagnetic Casimir interaction is also associated with an entropy that determines its limiting behaviour at high temperatures and/or large distances. The Casimir entropy for two material plates has recently attracted much interest also for low temperatures, as for certain situations a violation of the third law of thermodynamics (the Nernst theorem) has been claimed. This has been used to argue in favor of a description where the DC conductivity of the metallic plates is ignored. Although the result of this theoretical prescription provides a better fit to recent experiments, the situation is, however, not satisfactory from the physical point of view. In addition, a similar analysis for an experiment with laser-irradiated semiconductors leaves open the meaning of the threshold value above which the DC conductivity should be included in the theory.

Much has been said about spatially dispersive mirrors where the third law is verified, due to the anomalous skin effect, and where a continu-

§Present address: Theoretical Division, MS B213, Los Alamos National Laboratory, Los Alamos NM 87545, U. S. A.
ous cross-over from a dielectric to a perfectly conducting response has been found. We focus in these proceedings on a strictly local framework, mainly for simplicity, but also to show that this case is thermodynamically consistent as well. We shall see that, indeed, spatial dispersion plays only a small role in the range of wave vectors that are relevant for current Casimir experiments.

We take up the interpretation of Ref.10 where the nonzero Casimir entropy found as $T \to 0$ was associated to two oscillators coupled via a third one. Following this idea, we consider two half-spaces filled by an ideal electron gas, separated by a distance $L$, and provide a direct calculation of the entropy per area $S(L) = \lim_{T \to 0} S(L, T)$ in one of the two field polarizations. This calculation highlights the following point:

The Casimir entropy $S(L) < 0$ results from the coupling between two systems that are not in equilibrium as $T \to 0$. They are filled with a frozen magnetization and, in the local limit, have separately divergent (bulk and surface) entropies that characterize the disorder of the electromagnetic configuration. The Casimir entropy is the correction to additivity when the two bodies are close enough for their frozen currents to be mutually coupled by the quasi-static magnetic fields that ‘leak’ through their surfaces. The Nernst theorem is clearly not applicable for this disordered system. The situation is quite similar to the ‘ideal conductor’ (in distinction to a superconductor, see Ref.11) that does not reach thermodynamical equilibrium as it is cooled, because its random bulk currents freeze. (See Ref.12 where it is argued how special this ideal conductor case is.)

2. Casimir entropy from frozen medium currents

2.1. Motivation

We have analyzed in a recent paper\textsuperscript{13} the overdamped field modes to which the unusually large thermal corrections to the Casimir force between metals can be attributed. Substantiating previous observations\textsuperscript{14,15} we have interpreted the characteristic frequency, $\xi_L = D/L^2 = (\mu_0 \sigma L^2)^{-1}$, in terms of a diffusion equation (diffusion coefficient $D$) satisfied by the magnetic field and electric currents in a medium with DC conductivity $\sigma$.

There is no contradiction between thermodynamics and fluctuation electrodynamics in this case. Fields and currents induced in the metal are clearly damped and lose energy into the phonon bath, say. In equilibrium, however, this is compensated by field and current fluctuations that are created by the bath. This concept can be traced back to the Einstein–
Langevin theory of Brownian motion\textsuperscript{16} and is also the very essence of the fluctuation-dissipation theorem.\textsuperscript{17,18} Moreover, for the quantum field theory, the quantum (or zero-point) fluctuations of the bath variables are an essential tool to establish at all times the commutation relations for the field operators.\textsuperscript{19–23} In the field theory considered in Ref.13, we dealt with overdamped modes: if the wave equation were homogeneous, its eigenfrequencies would be purely imaginary, similar to free Brownian particles. The quantum theory of Brownian motion\textsuperscript{24} provides a consistent scheme for the quantum thermodynamics of this damped system. In this setting, nonzero entropies and even negative heat capacities find a quite natural explanation (see, e.g., Refs.25,26).

In the particular case of an ideal electron gas (or ‘perfect crystal’), the diffusion constant $D = D(T) = \mathcal{O}(T^2)$. As the temperature drops to zero, the diffusion-dominated modes of the electromagnetic field do not reach a unique ground state, but remain in the classical regime $\hbar \xi L \ll T$. This motivates the present calculation where the electromagnetic Casimir entropy between perfect crystals is re-derived within a classical model.

The basic ingredient are transverse modes that extend throughout the bulk of the gas: static current waves interlocked with a magnetic field. The magnetic fields associated to the bulk currents leave one medium, by continuity, and cross the vacuum gap to the other medium in the form of (transverse) evanescent waves. This coupling between the two media changes slightly the wave vector of each current mode. Summing over all modes, we get a non-zero change in entropy that depends, quite naturally, on the separation $L$. It represents the distance-dependent change per unit area of the (much larger) entropy of the two frozen bulk systems.

### 2.2. Lagrangian and conservation laws

We start with the Lagrangian density

$$\mathcal{L} = \frac{nm}{2} \dot{\xi}^2 + en\dot{\xi} \cdot A - \frac{1}{2\mu_0} (\nabla \times A)^2$$

(1)

where the field $\xi$ describes the displacement of a charged fluid element, $A$ is the vector potential, $n$ a constant background charge density and $e$ a coupling constant with units of charge. The current density is $\mathbf{j} = e n \dot{\xi}$ [see Eq.(2) below], so that $\dot{\xi}$ represents a velocity field. The first term in Eq.(1) is thus the kinetic energy (density), the second one a bilinear coupling, and the third one the magnetic energy. Note that we neglect electric fields here. This is consistent if we make the assumption that $\nabla \cdot \xi = \nabla \cdot A = 0$. The
first equality ensures that the medium displacement does not produce any charge density, the second one is the Coulomb gauge. The variation of the Lagrangian (1) with respect to $A$ gives the Faraday equation

$$en\dot{\xi} - \frac{1}{\mu_0} \nabla \times (\nabla \times A) = 0$$

(2)

In addition, the displacement field $\xi$ is a cyclic variable, hence we get a conserved momentum field

$$\frac{\partial \pi}{\partial t} = 0, \quad \pi = n m \dot{\xi} + e n A$$

(3)

There are two ways to implement this conservation law physically:

(i) In a London superconductor, the current density is tied at all times to the vector potential, with the momentum $\pi$ being zero:

$$\text{superconductor:} \quad j = en\dot{\xi} = -\frac{ne^2}{m} A$$

(4)

The Maxwell–Faraday equation (2) becomes

$$(\lambda^{-2} - \nabla^2) A = 0$$

(5)

where the Meißner–London penetration depth $\lambda$ is given by the familiar expression $\lambda^{-2} = \mu_0 ne^2/m = \Omega^2/c^2$ ($\Omega$ is the plasma frequency). Eq.(5) does only allow for solutions that start at the surface and exponentially decay into the bulk on a length scale $\lambda$ (or shorter). Except for a surface layer of thickness $\sim \lambda$, the interior of the medium remains free of magnetic field: the Meißner–Ochsenfeld effect.

From the London equation (4), we can also conclude that the Meißner effect is maintained in time-dependent fields (at least with sufficiently slow variations; a detailed analysis clearly goes beyond the simple model considered here). For a given frequency component $\omega$, the ‘dielectric function’ of the London superconductor can be read off from the polarization field associated to $\xi$:

$$P = en\xi = \frac{j}{-i\omega} = -\frac{\varepsilon_0 \Omega^2}{\omega^2} E$$

(6)

leading to the so-called plasma model $\varepsilon(\omega) = 1 - \Omega^2/\omega^2$. There is no violation of causality here, if we read Eq.(4) as a retarded response function between the current density and the time integral of the electric field (i.e., the vector potential).

The option (ii) that complies with the conservation law (3) corresponds to an ideal conductor:

$$\text{ideal conductor:} \quad \frac{\partial j}{\partial t} = 0 \quad \text{and} \quad \frac{\partial A}{\partial t} = 0$$

(7)
which means that currents, once created, are not damped and that the magnetic field is static. The value of the conserved momentum $\pi$ is not restricted otherwise. The Faraday equation (2) then yields the field $A$ in terms of its source $j$. Note that the magnetic field is in this case tied to the current density, similar to the scalar potential and the charge density in Coulomb-gauge electrodynamics. Let us switch to reciprocal space with wavevector $q$: the vector potential $A_q$ created by the current is

$$A_q = \mu_0 \frac{j_q}{q^2}$$  \hspace{1cm} (8)

so that the Lagrangian (1) becomes

$$L = \frac{\mu_0 V}{2} \sum_q \left( \lambda^2 + q^{-1} \right) |j_q|^2$$  \hspace{1cm} (9)

where $V$ is the quantization volume. The conjugate momentum becomes

$$\pi_q = \frac{m}{e} \left( 1 + \frac{1}{\lambda^2 q^2} \right) j_q$$  \hspace{1cm} (10)

### 2.3. Normal modes and entropy

The normal modes of the effective Lagrangian (9) can clearly be chosen as plane waves, labelled by wave vector $q$ and polarization index $\mu$. The associated Hamiltonian, expressed in terms of the canonical momentum field, is then

$$H = \frac{V}{2nm} \sum_{q,\mu} \left( 1 + \frac{1}{\lambda^2 q^2} \right)^{-1} |\pi_{q\mu}|^2$$  \hspace{1cm} (11)

The (classical) thermodynamics of this system is determined by summing the free energies of the normal modes over the quantum numbers $q, \mu$. For one mode, we find by calculating the classical partition function ($\beta = 1/T$)

$$F_{q\mu} = -T \log \int d\pi_{q\mu} \exp \left( -\frac{\beta}{2} \epsilon_q |\pi_{q\mu}|^2 \right) = \frac{T}{2} \log \frac{\beta \epsilon_q}{2\pi}$$  \hspace{1cm} (12)

where $\epsilon_q = (V/nm)(1 + \lambda^{-2}q^{-2})^{-1}$ determines the mode's energy. The entropy of this polarization mode is

$$S_{q\mu} = -\frac{\partial F_{q\mu}}{\partial T} = -\frac{1}{2} \log \frac{\beta \epsilon_q}{2\pi} + \frac{1}{2}$$  \hspace{1cm} (13)

where the equipartition term $+1/2$ comes from the $\beta$ in the logarithm.

When we sum this over all modes, the entropy becomes to leading order extensive in the volume $V$ of the medium. The part that depends on the
surface is calculated in the usual way. Consider two media (total volume \( V \)) with parallel surfaces of area \( A \) facing each other at a distance \( L \) and write the entropy of the total system in the form

\[
S = V s + 2AS_{\text{surf}} + AS(L) \quad (14)
\]
where \( s \) is the (intensive) bulk entropy density, \( S_{\text{surf}} \) is the entropy per area of one (isolated) surface and \( S(L) \) the Casimir entropy per area. We can read the latter as the deviation from additivity in the system of two media: it thus describes how the disorder (or information content) of the two plates is changed by the coupling across the vacuum gap of thickness \( L \).

The physical mechanism for this coupling is the penetration of magnetic fields through the medium surface, as allowed for by the electromagnetic boundary conditions. In the vacuum between the media, the fields satisfy the Laplace equation \( \nabla^2 A = 0 \): for a given wave vector \( k \) parallel to the surface, they ‘propagate’ perpendicular to the surface (along the \( z \)-axis, say) as evanescent waves \( \sim \exp(\pm kz) \) where \( k = |k| \). For a single surface, only solutions that decay into the vacuum are permitted. In the gap \( 0 \leq z \leq L \) between two surfaces, even and odd solutions \( \cosh k(z - L/2) \) and \( \sinh k(z - L/2) \) can be constructed. This is illustrated schematically in Fig. 1.

![Fig. 1. Illustration of standing waves at the surface of an ideally conducting medium. We plot the component of the vector potential tangential to the surface. Thin line: isolated surface, thick line: mode between two surfaces with even parity.](image-url)

Both the surface entropy and the Casimir entropy can be calculated from the phase shifts of standing wave modes (see Refs.29,30 for details). For the surface entropy,

\[
S_{\text{surf}} = \sum_\mu \int \frac{d^2k}{(2\pi)^2} \int_0^\infty dk z S_{\text{q}\mu} \left( -\frac{1}{\pi} \frac{\partial \theta_\mu}{\partial k z} \right) \quad (15)
\]
where \( q = (k, k_z) \), and the mode functions in the medium \( (z \leq 0) \) are proportional to \( e^{ikr} \sin(k_z z + \theta_{\mu}) \) with \( r_\parallel = (x, y) \) the coordinates parallel to the surface. From this form, we can also read off a ‘reflection coefficient’ for (time-independent) waves from within the medium, \( r_{\mu} = -e^{-2i\theta_{\mu}} \). From a physical point of view, we can interpret the phase derivative in Eq.(15) as a density of modes in \( q \)-space, more precisely, its change due to the surface.

For an isolated interface, the usual matching of the component of the vector potential tangential to the surface and its derivative at the interface yields in TE-polarization (current perpendicular to the plane of incidence spanned by \( k \) and the surface normal)

\[
\tan \theta_{TE} = -\frac{k_z}{k} \quad \text{and} \quad r_{TE} = \frac{k_z - ik}{k_z + ik}
\]

Here, \( k = |k| \) gives the decay constant of the evanescent wave on the vacuum side. In the TM-polarization (current in the plane of incidence), the current has to satisfy the boundary condition \( \lim_{z \to 0} j_z(z) = 0 \) to avoid the build-up of a surface charge sheet. (That case would require electrical field energy in the Lagrangian (1) and is best described within a spatially dispersive model.) This boundary condition immediately leads to \( r_{TM} = 1 \), and there is no phase shift. The surface entropy in TM-polarization hence vanishes, while it is logarithmically divergent at large \( q \) in the TE-polarization:

\[
S_{surf} \approx -\frac{8\pi\lambda^2}{q_c \lambda} \quad \text{with a short-range cutoff } q_c.
\]

One needs a non-local description of the material response (spatial dispersion) to get a finite result, see, e.g., Ref.31 for the surface self-energy.

For the Casimir entropy, a local calculation is sufficient, as we shall see now: the reflection phases for even and odd modes in the vacuum gap are found as (we henceforward suppress the TE-polarization label)

\[
\tan \theta_{even}(L) = -\frac{k_z}{k} \coth \frac{kL}{2}, \quad \tan \theta_{odd}(L) = -\frac{k_z}{k} \tanh \frac{kL}{2}
\]

The entropy per area for the two-surface system, \( 2S_{surf} + S(L) \), is then given by Eq.(15) with \( \theta \) replaced by \( \theta_{even}(L) + \theta_{odd}(L) \). Subtract twice the single-interface phase shift and calculate the quantity

\[
\exp 2i[\theta_{even}(L) + \theta_{odd}(L) - 2\theta] = \frac{1 - r^2 e^{-2kL}}{1 - (r^*)^2 e^{-2kL}}
\]

as can be checked with straightforward algebra. The Casimir entropy from
TE-polarized bulk currents becomes [combining Eqs.(13, 15, 18)]

\[ S(L) = \int_0^\infty \frac{k \, dk}{2\pi} \int_0^\infty \frac{dz}{2\pi} \left( \log \frac{2V\lambda^2q^2}{2\pi n m (1 + \lambda^2 q^2)} - 1 \right) \frac{\partial}{\partial k_z} \text{Im} \log (1 - r^2 e^{-2kL}) \]

(19)

The terms independent of \( k_z \) in the entropy per mode are irrelevant: after a partial integration, the integrated terms vanish because for \( k_z \to 0, \infty \), the reflection coefficient \( r \) becomes real. Manifestly, short-wavelength modes with \( 2kL \gg 1 \) are suppressed, and a local theory is sufficient unless \( L \) becomes comparable to the length scales typical for spatial dispersion (mean free path, Debye-Hückel screening length, Fermi wavelength).

2.4. Calculation of the entropy

Integrating Eq.(19) by parts, we have to evaluate the integral:

\[ I_k = - \int_{-\infty}^{\infty} \frac{dk_z}{2\pi \lambda^2 (k_z^2 + k^2)(k_z^2 + k^2 + \lambda^2)} k_z \log (1 - r^2 e^{-2kL}) \]

(20)

where we recall that \( r \) is given by Eq.(16) above. We have extended the integration domain to \( -\infty < k_z < +\infty \), using the property \( r(-k_z) = [r(k_z)]^* \). Observe that \( r(k_z) \), as a function of complex \( k_z \), satisfies \( |r(k_z)| \leq 1 \) in the upper half-plane, that the integrand vanishes at infinity, and evaluate the integral by closing the contour. There are simple poles at \( k_z = i k \) and \( k_z = i(k^2 + \lambda^{-2})^{1/2} \). At the first pole, the reflection coefficient (16) vanishes, and we get from the second one:

\[ I_k = \frac{1}{2} \log \left[ 1 - r_{pl}^2(k, 0) e^{-2kL} \right], \quad r_{pl}(k, 0) = \frac{(k^2 + \lambda^{-2})^{1/2} - k}{(k^2 + \lambda^{-2})^{1/2} + k} \]

(21)

As it happens, the reflection coefficient \( r_{pl}(k, \omega) \) for electromagnetic waves from a plasma half-space [dielectric function after Eq.(6)] appears here, evaluated at zero frequency and in the TE-polarization. If Eq.(21) is integrated over \( k \), we get the ‘entropy defect’ calculated in the Lifshitz theory of the Casimir effect using the local dielectric function of a ‘perfect crystal’ [see, e.g., Eq.(20) of Ref.5]:

\[ S(L) = \int_0^\infty \frac{k \, dk}{2\pi} I_k = \int_0^\infty \frac{dk}{2\pi} \log \left[ 1 - r_{pl}^2(k, 0) e^{-2kL} \right] \]

(22)

A switch to the integration variable to \( y = 2kL \) shows that

\[ S(L) = - \frac{\zeta(3)}{16\pi} \frac{f(L/\lambda)}{L^2} \]

(23)
where the scaling function \( f(L/\lambda) \), plotted in Fig. 2, is dimensionless and normalized to unity in the limit \( L \gg \lambda \). Indeed, in this regime, one may expand \( r_{pl}(k,0) \) in powers of \( k \) to get the asymptotic series [for higher terms, see Eq. (20) of Ref. 5]:

\[
L \gg \lambda : \quad f(L/\lambda) \approx 1 - 4\frac{\lambda}{L} + 12\frac{\lambda^2}{L^2} + \mathcal{O}(\lambda/L^3)
\] (24)

3. Conclusions

We have analyzed the Casimir entropy for the ideal electron gas, in particular the contribution of electric currents frozen inside the bulk. This system shows (electromagnetic) disorder, and the third law of thermodynamics does not apply in its orthodox formulation. We have recovered the ‘entropy defect’ (negative Casimir entropy at zero temperature) reported in several places in the literature. Its thermodynamically consistent interpretation is the measure of the change in the disorder of the frozen currents due to their interaction through quasi-static magnetic fields.

Acknowledgments. We acknowledge financial support by the European Science Foundation within the activity ‘New Trends and Applications of the Casimir Effect’ (www.casimir-network.com), F.I. acknowledges financial support by the Alexander von Humboldt Foundation.
References

1. A. Gambassi, C. Hertlein, L. Helden, S. Dietrich and C. Bechinger, Europhys. News 40, 18 (Jan 2009).
2. R. Balian and B. Duplantier, Ann. Phys. (N. Y.) 112, 165 (1978).
3. J. Feinberg, A. Mann and M. Revzen, Ann. Phys. (N. Y.) 288, 103 (2001).
4. G. L. Klimchitskaya and V. M. Mostepanenko, Phys. Rev. A 63, 062108 (2001).
5. V. B. Bezerra, G. L. Klimchitskaya, V. M. Mostepanenko and C. Romero, Phys. Rev. A 69, 022119 (2004).
6. R. Decca, D. López, E. Fischbach, G. Klimchitskaya, D. Krause and V. Mostepanenko, Eur. Phys. J. C 51, 963 (2007).
7. F. Chen, G. L. Klimchitskaya, V. M. Mostepanenko and U. Mohideen, Phys. Rev. B 76, 035338 (2007).
8. V. B. Svetovoy, Phys. Rev. Lett. 101, 163603 (2008).
9. L. P. Pitaevskii, Phys. Rev. Lett. 101, 163202 (2008).
10. J. S. Hoye, I. Brevik, J. B. Aarseth and K. A. Milton, Phys. Rev. E 67, 056116 (2003).
11. L. D. Landau, E. M. Lifshitz and L. P. Pitaevskii, Electrodynamics of continuous media, 2nd edn. (Pergamon, Oxford, 1984).
12. W. A. B. Evans and G. Rickayzen, Ann. Phys. (N. Y.) 33, 275 (1965).
13. F. Intravaia and C. Henkel, Phys. Rev. Lett. 103, 130405 (2009).
14. J. R. Torgerson and S. K. Lamoreaux, Phys. Rev. E 70, 047102 (2004).
15. V. B. Svetovoy, Phys. Rev. A 76, 062102 (2007).
16. A. Einstein, Ann. Physik (Leipzig), Vierte Folge 17, 549 (1905).
17. H. B. Callen and T. A. Welton, Phys. Rev. 83, 34 (1951).
18. X. L. Li, G. W. Ford and R. F. O’Connell, Phys. Rev. E 48, 1547 (1993).
19. B. Huttner and S. M. Barnett, Europhys. Lett. 18, 487 (1992).
20. T. Gruner and D.-G. Welsch, Phys. Rev. A 51, 3246 (1995).
21. A. Tip, Phys. Rev. A 56, 5022 (1997).
22. L. G. Suttorp, J. Phys. A: Math. Gen. 40, 3697 (2007).
23. S. Scheel and S. Y. Buhmann, Acta Phys. Slov. 58, 675 (2008).
24. U. Weiss, Quantum Dissipative Systems, Series in Modern Condensed Matter Physics, Vol. 10, third edn. (World Scientific, Singapore, 2007).
25. G.-L. Ingold, P. Hänggi and P. Talkner, Phys. Rev. E 79, 061105 (2009).
26. G.-L. Ingold, A. Lambrecht and S. Reynaud, Phys. Rev. E 80, 041113 (2009).
27. F. London and H. London, Proc. Roy. Soc. (London) A 149, 71 (1935).
28. C. Cohen-Tannoudji, J. Dupont-Roc and G. Grynberg, Photons and Atoms - Introduction to Quantum Electrodynamics (Wiley, New York 1989).
29. G. Barton, Rep. Prog. Phys. 42, 963 (1979).
30. M. Bordag, U. Mohideen and V. M. Mostepanenko, Phys. Rep. 353, 1 (2001).
31. N. J. Morgenstern Horing, E. Kamen and G. Gumbs, Phys. Rev. B 31, 8269 (1985).