Radiative Phase Transitions and Casimir Effect Instabilities

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Molecular quantum electrodynamics leads to photon frequency shifts and thus to changes in condensed matter free energies often called the Casimir effect. Strong quantum electrodynamics coupling between radiation and molecular motions can lead to an instability beyond which one or more photon oscillators undergo a displacement phase transition. The phase boundary of the transition can be located by a Casimir free energy instability.

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I. INTRODUCTION

The interaction between electromagnetic field and the molecules of condensed matter shifts the frequency of the photon oscillators which changes the free energy of the condensed matter system. This free energy shift is known as the Casimir effect[1]. From a quantum field theoretical viewpoint, the Casimir free energy is the contribution due to one photon loop Feynman diagrams[2]. Originally, Casimir intended to describe either photon oscillator induced forces between a few atoms or between fixed perfect conductors. Presently Casimir effects include the dielectric and paramagnetic materials as well as irreversible effects in moving conductors[3, 4, 5, 6]. The literature is quite extensive but several excellent reviews are available[7, 8, 9]. Our purpose is to point out views are available[7, 8, 9]. Our purpose is to point out that if the coupling between the photon oscillators and the molecules is sufficiently strong, then the photon oscillators undergo a displacement into a coherent electromagnetic radiation state. While the single photon loops do not describe the nature of the radiation coherence, the phase boundary between the normal radiation state and the coherent radiation state can be located as a free energy instability. As the thermodynamic equation of state boundary of the normal photon oscillator regime is approached, one or more of the photon oscillator frequencies tends toward zero. Such zero frequency modes lead to a Casimir free energy signature of the forthcoming radiation transition.

In Sec.II the connection between the change in the photon density of states free energy and the photon scattering phase shift is reviewed. The Casimir free energy then follows by directly superimposing the Planck free energies of the shifted oscillators. In Sec.III the free energy is expressed directly in terms of the (gauge invariant) electric field photon propagator $G$ and the dielectric susceptibility $\chi$. The Casimir instability is explored in Sec.IV (eventually in terms of the dielectric response function $\varepsilon$). The phase regime of the Casimir photon oscillator stability is shown to be identical to the phase regime of the stable Clausius-Mossotti theory[10, 11]. The general physical principles involved are discussed in the concluding Sec.V.

II. PHOTON SCATTERING OPERATOR

Consider a condensed matter object which can elastically scatter photons. Mathematically the scattering of a photon having frequency $\omega$ would be described by a unitary scattering operator $S(\omega)$ whose eigenvalues determine a set of phase shifts $\{\delta_\nu(\omega)\}$ via

$$S(\omega^2)\ket{\nu} = e^{2i\delta_\nu(\omega)}\ket{\nu}. \quad (1)$$

The Wigner time delay[12] $\tau_\nu(\omega)$ in a photon scattering channel $\nu$ represents the extra amount of time the photon remains in the neighborhood of the target due to the photon-target interaction. It is well known to obey

$$\tau_\nu(\omega) = \frac{2d\delta_\nu(\omega)}{d\omega}. \quad (2)$$

If one sums the time delays over all the channels, then one may compute the extra number $dN(\omega)$ of photon states in a bandwidth $d\omega$ due the target-photon interaction

$$dN(\omega) = \frac{1}{2\pi} \sum_\nu \tau_\nu(\omega) d\omega = \frac{1}{\pi} \sum_\nu d\delta_\nu(\omega). \quad (3)$$

The Casimir contribution to the condensed matter object free energy may be written in terms of the free energy $f(\omega,T)$ of a simple harmonic oscillator; i.e.

$$f(\omega,T) = -k_B T \ln \left\{ \sum_{N=0}^{\infty} e^{-(N+1/2)\hbar \omega/k_B T} \right\}$$

$$= k_B T \ln \left\{ 2 \sinh \left( \frac{\hbar \omega}{2k_B T} \right) \right\},$$

$$\frac{\partial f(\omega,T)}{\partial \omega} = \frac{\hbar}{2} \coth \left( \frac{\hbar \omega}{2k_B T} \right) = k_B T \sum_{n=-\infty}^{\infty} \frac{\omega}{\omega_n^2 + \omega^2},$$

$$\omega_n = \left( \frac{2\pi k_B T}{\hbar} \right) n, \quad n = 0, \pm 1, \pm 2, \ldots.$$ \quad (4)

The Casimir free energy is found by simply summing oscillator free energies over all the added photon modes as dictated by Eqs.(3) and (4). It is

$$\Delta F = \int_0^\infty f(\omega,T) dN(\omega) = -\int_0^\infty \frac{\partial f(\omega,T)}{\partial \omega} N(\omega) d\omega,$$
\[ \Delta F = -k_BT \sum_{n=-\infty}^{\infty} \int_0^\infty \frac{\omega N(\omega) d\omega}{\omega^2 + \omega_n^2} \]
\[ = -k_BT \sum_{n=-\infty}^{\infty} \int_0^\infty \frac{\omega \sum_{\delta_n(\omega)} d\omega}{\omega^2 + \omega_n^2}. \tag{5} \]

Now consider the analytic continuation from real frequency \( \omega \) to the complex frequency \( \zeta \) in the upper half plane
\[ \zeta = \omega + is \quad \text{where} \quad s \equiv \Im \zeta \geq 0. \tag{6} \]

The analytically continued scattering operator obeys the dispersion relation
\[ \ln \det S(\zeta^2) = \frac{2}{\pi} \int_0^\infty \omega \Im \ln \det S(\omega^2 + i\omega) d\omega, \]
\[ \ln \det S(\zeta^2) = \frac{4}{\pi} \int_0^\infty \omega \sum_{\delta_n(\omega)} d\omega. \tag{7} \]

Our final expression for the Casimir free energy in terms of the analytically continued scattering operator follows from Eqs. \( \text{5} \) and \( \text{7} \) to be
\[ \Delta F = -\frac{k_BT}{4} \sum_{n=-\infty}^{\infty} \ln \det S(-\omega_n^2). \tag{8} \]

Let us now consider the more general case wherein the scattering operator may also describe inelastic processes such as photon absorption by the condensed matter sample. The eigenvalue problem, \( S|\nu\rangle = e^{2i\Delta_\nu} |\nu\rangle \), now yields complex phase shifts with \( \Im \Delta_\nu \geq 0 \). However, the Casimir free energy Eq. \( \text{8} \) remains in tact. This is most easily understood in terms of the photon propagator.

### III. PHOTON PROPAGATORS

Starting from Maxwell’s equations
\[ \text{curl}\mathbf{E} = -\frac{1}{c} \left( \frac{\partial \mathbf{B}}{\partial t} \right), \]
\[ \text{curl}\mathbf{B} = \frac{1}{c} \left( \frac{\partial \mathbf{E}}{\partial t} \right) + 4\pi \mathbf{J}, \]
\[ \text{div}\mathbf{E} = 4\pi \rho \quad \text{and} \quad \text{div}\mathbf{B} = 0, \tag{9} \]
one finds that
\[ \left\{ \frac{1}{c^2} \left( \frac{\partial}{\partial t} \right)^2 - \Delta \right\} \mathbf{E} = -4\pi \left\{ \frac{1}{c^2} \frac{\partial \mathbf{J}}{\partial t} + \text{grad}\rho \right\}. \tag{10} \]

For any locally conserved charge \( (\partial \rho/\partial t) + \text{div}\mathbf{J} = 0 \), there exists a polarization \( \mathbf{P} \) such that
\[ \rho = -\text{div}\mathbf{P} \quad \text{and} \quad \mathbf{J} = \frac{\partial \mathbf{P}}{\partial t}. \tag{11} \]
If we invoke the retarded tensor propagator
\[ \mathbf{G}(\mathbf{r}, \zeta) = \left\{ \frac{\zeta}{c} e^{i\zeta r/c} \right\} \left( 1 + \nabla \nabla \right) \frac{e^{i\zeta r/c}}{r} \quad \text{for} \quad \Im \zeta > 0, \tag{12} \]
then Eqs. \( \text{10} \) and \( \text{11} \) are formally solved by
\[ \mathbf{E}(\mathbf{r}, t) = \mathbf{E}_{in}(\mathbf{r}, t) + \int G(\mathbf{r}-\mathbf{r}', \zeta = i\frac{\partial}{\partial t}) \cdot \mathbf{P}(\mathbf{r}', t)d^3\mathbf{r}', \tag{13} \]
wherein the incoming photon is described by an electric field obeying the vacuum wave equation
\[ \left\{ \frac{1}{c^2} \left( \frac{\partial}{\partial t} \right)^2 - \Delta \right\} \mathbf{E}_{in} = 0, \tag{14} \]
and the outgoing photon has been scattered by the polarization \( \mathbf{P} \). The use of the formal operator replacement \( \zeta = i(\partial/\partial t) \) may be illustrated as follows: The polarization response in the condensed matter target may be related to the electric field by employing a retarded non-local response function
\[ \mathbf{P}(\mathbf{r}, t) = \int_0^\infty \int K(\mathbf{r}, \mathbf{r}', s) \cdot \mathbf{E}(\mathbf{r}', t-s)d^3\mathbf{r}'ds, \]
\[ \mathbf{P}(\mathbf{r}, t) = \int \left[ \int_0^\infty K(\mathbf{r}, \mathbf{r}', s)e^{-s(\partial/\partial t)} ds \right] \cdot \mathbf{E}(\mathbf{r}', t)d^3\mathbf{r}', \tag{15} \]
with the complex frequency dependent susceptibility defined as
\[ \chi(\mathbf{r}, \mathbf{r}', \zeta) = \int_0^\infty K(\mathbf{r}, \mathbf{r}', s)e^{i\zeta s}ds. \tag{16} \]

The scattering equation follows from Eqs. \( \text{13} \) and \( \text{15} \) to be
\[ \mathbf{E}(\mathbf{r}, t) = \mathbf{E}_{in}(\mathbf{r}, t) + \int \int G(\mathbf{r}-\mathbf{r}', \zeta = i\frac{\partial}{\partial t}) \cdot \chi(\mathbf{r}', \mathbf{r}'', \zeta = i\frac{\partial}{\partial t}) \cdot \mathbf{E}(\mathbf{r}'', t)d^3\mathbf{r}'d^3\mathbf{r}''. \tag{17} \]

The Fredholm-Jost determinant \([13, 14]\) \( J(\zeta) \) and its logarithmic determinant \( \Phi(\zeta) \) for the scattering integral Eq. \( \text{17} \) are defined as
\[ J(\zeta) = \det \{ 1 - G(\zeta)\chi(\zeta) \}, \]
\[ \Phi(\zeta) = -\ln J(\zeta) = -Tr \ln \{ 1 - G(\zeta)\chi(\zeta) \}. \tag{18} \]

Eq. \( \text{18} \) is related to the determinant of the scattering operator according to
\[ \det S(\zeta^2) = -\left[ \frac{J(\zeta)}{J(-\zeta)} \right]. \tag{19} \]
From Eqs. \( \text{8} \), \( \text{18} \) and \( \text{19} \) it then follows that
\[ \Delta F = -\frac{k_B T}{2} \sum_{n=-\infty}^{\infty} \Phi(i|\omega_n|), \]
\[ \Phi(\zeta) = \sum_{k=1}^{\infty} \frac{1}{k} Tr \{ G(\zeta) \chi(\zeta)^j \}^k. \]  

Eqs. (20) yield the “one loop” contribution to the free energy which constitutes the Casimir effect. The Feynman diagrams are shown in Fig. 1. If one employs the eigenvalue equation for a photon state \(|\nu\rangle\),

\[ G(\zeta) \chi(\zeta) |\nu\rangle = \eta_\nu(\zeta) |\nu\rangle, \]  

then

\[ \Phi(\zeta) = \sum_{\nu} \sum_{k=1}^{\infty} \frac{\eta_\nu(\zeta)^k}{k} = - \sum_{\nu} \ln \left( 1 - \eta_\nu(\zeta) \right). \]  

For the Casimir free energy \(\Delta F\) in Eqs. (20) and (22) to be stable, it is necessary for the eigenvalues to obey the condition

\[ \eta_\nu(i|\omega_n|) < 1 \text{ for all } \nu \text{ and } n, \quad \text{(Stable)}. \]  

If any eigenvalue (say as a function of temperature) passes through unity, then the Casimir free energy will have an imaginary part. The transition rate per unit time for the system to make a transition into a stable state is given by \(\Gamma = -(2/\hbar) \Im m \Delta F\). The Casimir one photon loop free energy in Fig. 1 is not sufficient for computing the free energy of the stable ordered radiative phase. Nevertheless, by examining the eigenvalue Eq. (21) equation for the mode, i.e., channel \(|\nu\rangle\), which becomes unstable, one may gain insights into the radiative coherent state which will be stabilized. The phase diagram for the disordered to ordered radiative state may also be computed. Let us illustrate how this comes about.

**IV. POLARIZATION INSTABILITY**

From Eqs. (12), (15) and (21) one may examine the electric field of a channel mode \(|\nu\rangle\) according to

\[ \int \int G(r - r', \zeta) \cdot \chi(r', r'', \zeta) \cdot E_\nu(r'') d^3r' d^3r'' = \eta_\nu(\zeta) E_\nu(r) \]  

Eq. (24) can be decomposed into two parts: (i) The mode \(E_\nu(r)\) produces a polarization \(P_\nu(r)\). (ii) The polarization \(P_\nu(r)\) radiates the electric field \(E_\nu(r)\).

\[ \int \chi(r - r'', \zeta) \cdot E_\nu(r') d^3r' = \eta_\nu(\zeta) P_\nu(r), \]
\[ \int G(r - r', \zeta) \cdot P_\nu(r') d^3r' = E_\nu(r). \]  

If the eigenvalue \(\eta\) passes through unity, then the field mode can be sustained self consistently indicating a radiative instability. Otherwise, the coupling is too weak to maintain the mode and the Casimir free energy contribution is stable.

To see what is involved, let us consider a translational invariant fluid for which the bulk Casimir free energy per unit volume \(\Delta f\) is determined by electric susceptibility

\[ \chi(r - r', \zeta) = \int \chi_k(\zeta) e^{ik(r - r')} \frac{d^3k}{(2\pi)^3}. \]  

In detail, Eqs. (12), (20), (22), (25), and (26) imply

\[ E(r; k) = E_k e^{ikr}, \]
\[ G_k(\zeta) = \int G(r, \zeta) e^{-ikr} d^3r \]
\[ = -4\pi \left\{ \frac{kk}{k^2 - (\zeta/\epsilon)^2} \right\}, \]
\[ \eta_k(\zeta) E_k = G_k(\zeta) \cdot \chi_k(\zeta) \cdot E_k, \]
\[ \frac{2\Delta f}{k_B T} = -\sum_{n=-\infty}^{\infty} \int \ln \left( 1 - \eta_k(i|\omega_n|) \right) \frac{d^3k}{(2\pi)^3}. \]  

The static \((\omega_n = 0)\) contribution to the free energy per unit volume in Eq. (27) is then determined by

\[ \varepsilon(k) = 1 - \eta_k(0) \]
\[ \Delta f_{static} = -\frac{k_B T}{2} \int \ln \varepsilon(k) \frac{d^3k}{(2\pi)^3}, \]
\[ \varepsilon(k) = 1 + 4\pi \left( \frac{\kappa \cdot \chi_k(0) \cdot \kappa}{k^2} \right) = 1 + 4\pi \chi(0) \]  

Let us examine Eqs. (12) and (24) in the limit of zero frequency; i.e.

\[ \lim_{\zeta \to 0} G(r - r', \zeta) = \nabla \nabla \left( \frac{1}{|r - r'|} \right), \]
\[ \lim_{\zeta \to 0} G(r - r', \zeta) = D(r - r') - \frac{4\pi}{3} \delta(r - r'), \]
\[ D(r) = \left\{ \frac{3rr - r^2}{r^3} \right\}, \]
\[ E_k(r) = \int D(r - r') \cdot P_k(r') d^3r' - \left( \frac{4\pi}{3} \right) P_k(r). \]  

**FIG. 1**: Shown are the one loop Feynman diagrams contributing to the Casimir free energy in Eq. (24). For each propagator wavy line one inserts \(G_{ij}(r, r, \zeta)\) in accordance with Eq. (12). For each “self energy part” one inserts \(\chi_{ij}(r, r, \zeta)\) in accordance with Eqs. (15) and (16). The trace “\(Tr\)” includes sums over polarization indices and integrals over space.
A static polarization will produce a local dipolar electric field $\mathbf{F}(\mathbf{r}; \mathbf{k})$ via

$$
\mathbf{F}(\mathbf{r}; \mathbf{k}) = \int \mathbf{D}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}'; \mathbf{k}) d^3 \mathbf{r}', \\
\mathbf{F}(\mathbf{r}; \mathbf{k}) = \mathbf{E}(\mathbf{r}; \mathbf{k}) + \left( \frac{4\pi}{3} \right) \mathbf{P}(\mathbf{r}; \mathbf{k}).
$$

(30)

Eqs. (30) and (31) imply the dielectric response function $\beta$ for a fluid with a volume per molecule of $v$ and a nonlocal molecular polarizability $\beta(\mathbf{k})$, defined by the local field $\mathbf{F}$,

$$
v \mathbf{P}(\mathbf{r}; \mathbf{k}) = \beta(\mathbf{k}) \mathbf{F}(\mathbf{r}; \mathbf{k}),
$$

(31)

For a fluid with a volume per molecule of $v$ and a nonlocal molecular polarizability $\beta(\mathbf{k})$, defined by the local field $\mathbf{F}$,

$$
\lim_{|\mathbf{k}| \to 0} \beta(\mathbf{k}) = \alpha \quad \text{(polarizability)},
$$

$$
\lim_{|\mathbf{k}| \to 0} \varepsilon(\mathbf{k}) = \varepsilon \quad \text{(dielectric constant)},
$$

$$
\varepsilon = \frac{3v + 8\pi \alpha}{3v - 4\pi \alpha}.
$$

(33)

The Clausius-Mossotti stability condition, if $3v > 4\pi \alpha$ (stable normal phase),

$$
3v > 4\pi \alpha \quad \text{(stable normal phase)},
$$

(34)

has then been shown to follow from the Casimir effect stability ($\eta < 1$).

V. CONCLUSIONS

The quantum electrodynamic interaction between molecules and photons gives rise to frequency Lamb shifts which in turn contribute to a shift in the free energy of a condensed matter system. This Casimir contribution to the free energy can become unstable if the interaction coupling is too strong. The instability is the signature to a phase transition into a state with coherent radiation. We have exhibited such an instability within the above statistical thermodynamic considerations. We conclude this work by exhibiting the instability directly in terms of a collective Lamb shift.

For zero wave number ($\mathbf{k} = 0$) but finite frequency ($\omega \neq 0$), the dielectric response function of Eq. (32) reads

$$
\varepsilon(\omega) = \frac{1 + \{8\pi \beta(\omega)/3v\}}{1 - \{4\pi \beta(\omega)/3v\}}.
$$

(35)

If the molecular polarizability $\beta(\omega)$ can be described by a single excitation frequency $\omega_0 = (\Delta E/\hbar)$ via

$$
\beta(\omega) = \left( \frac{\omega_0^2}{\omega^2 - \omega_0^2} \right) \alpha,
$$

(36)

gives rise to a shifted frequency

$$
\omega_0^2 = \omega_0^2 \left\{ 1 - \frac{4\pi \alpha}{3v} \right\} \quad \text{(collective Lamb Shift).}
$$

(38)

The Eq. (34) for the stable phase regime requires that the collective Lamb shifted frequency $\Omega_0$ be real. A strong coupling imaginary frequency is a clear indicator of an unstable radiation phase.

While the Casimir effect expressions are sufficient to derive the stable photon oscillator regime in temperature and density, the one photon loop approximation lacks the sensitivity to decide the nature of the radiation ordered state. Ordered states of matter are not easily understood from a perturbation theory viewpoint.

[1] H.B.G. Casimir and D. Polder, Phys. Rev. 106, 1117 (1957).
[2] A.A. Abrikosov, L.P. Gorkov and I.E. Dzyaloshinski, Methods of Quantum Field Theory in Statistical Physics, Dover Publications, New York (1975).
[3] E. Sassaroli, Y.N. Srivastava, J. Swain and A. Widom, “The Dynamical and Static Casimir Effects and the Thermodynamic Instability” in Comments on Atomic and Molecular Physics, Eds. J.F. Bab, P.W. Milonni and L. Spruch, OPA N.V. (2000).
[4] G.T. Moore, J. Math. Phys. 11, 2679 (1970).
[5] S.A. Fulling and P.C.W. Davies, Proc. Roy. Soc. Lond. A 348, 393 (1976).
[6] V.V. Dodonov and A.B. Klimov, Phys. Rev. A53, 2664 (1996).
[7] S.K. Lamoreaux, Phys. Rev. Lett. 78, 5 (1997).
[8] M. Bordag, U. Mohideen and V. M. Mostepanenko, Phys. Rept. 353, 1 (2001).
[9] K.A. Milton, “The Casimir Effect, Physical Manifestations of Zero-Point Energy”, World Scientific, Singapore, (2001).
[10] O.F. Mossotti, Memorie Mat. Fis. Modena 24, 49 (1850).
[11] R. Clausius, Die mechanische W. armtheorie II, 62 Braunschweig (1897).
[12] E.P. Wigner, Phys. Rev. 98, 145 (1955).
[13] R.G. Newton, Scattering Theory of Waves and Particles,
2nd ed. Springer-Verlag, New York, (1982).

[14] R. Jost and A. Pais, *Phys. Rev.* **82**, 840 (1951).

[15] S. Sivasubramanian, A. Widom and Y.N. Srivastava, *Mod. Phys. Lett.* **B16**, 1201 (2002).

[16] S. Sivasubramanian, A. Widom and Y.N. Srivastava, arXiv:cond-mat/0301613

[17] W.E. Lamb and R.C. Retherford, *Phys. Rev.* **72**, 241 (1947).