The Physics of Atom–Surface Interactions
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In this lecture, an overview on interactions between atoms and surfaces is given that are mediated by the electromagnetic field. The emphasis is on dispersion (or van der Waals) forces and transitions induced by thermal fluctuations in the near field of a surface. Applications with cold atoms held in microscopic traps near surfaces, as outlined in the lecture by J. Schmiedmayer, provide the experimental background for this theory lecture.

We do not cover the chemical physics aspects that are relevant at distances comparable to the atomic scale. Phenomena like adsorption and diffusion on surfaces, or atomic beam diffraction from crystalline surfaces, are left to the lectures by J. Frenken and H. Lezec.

Outline

First part: forces

• Theory of the Van der Waals interaction. Electric dipole coupling, force from electromagnetic field fluctuations.

• Characterization of the field near a surface. Cross spectral density, fluctuation-dissipation theorem, example: planar surface.

• Discussion of the Van der Waals–Casimir force. Asymptotic calculation of the near field spectral density.

Second part: transitions

• Quantum states relevant for atoms

• Fermi’s Golden Rule, connection to the cross spectral density

• Rates for different processes, scaling laws.
1 Van der Waals Forces

1.1 Conventional viewpoint

The Van der Waals force derives from the energy shift an atomic ground state experiences in front of a surface. This shift is computed in second order perturbation theory, coupling the atom to the mode continuum of the electromagnetic field. The following section (in small characters like these) is taken from the lecture notes “Theoretical Quantum Optics I”, held at Universität Potsdam (Germany) winter semester 2003/04. The complete notes are online at www.quantum.physik.uni-potsdam.de.

1.1.1 Single-mode vacuum shift

Let us start with a single mode of the electromagnetic field. We have seen previously that the ground state $|g; 0\rangle$ of the atom+field system is not affected by the interaction. This is actually only true in the rotating wave approximation. When we include the nonresonant terms\(^{1}\),

$$H_{nr} = \hbar g (\sigma_+ a + \sigma_- a)$$

they do affect the ground state, since

$$H_{nr} |g; 0\rangle = \hbar g |e; 1\rangle.$$

In second order perturbation theory, we therefore get the following energy shift

$$\delta E_{g0} = - \frac{|\langle e; 1|H_{nr}|g; 0\rangle|^2}{E_{e1} - E_{g0}} = - \frac{\hbar^2 g^2}{\hbar (\omega_A + \omega)} \quad (1)$$

This shift is very small compared to those due to the resonant interaction because here the “detuning” $\omega_A + \omega$ is large (the transition can only happen “virtually” because it violates energy conservation).

Nevertheless, we learn that the atom-field interaction does displace the absolute ground state of the system, even for a single mode. The Lamb shift is the generalization of this result for the full, multi-mode electromagnetic field.

1.1.2 Lamb shift, a first glimpse

The calculation of the Lamb shift is a basic example of the different infinities that occur in quantum electrodynamics. We only give a first idea of the calculation, without

\(^{1}g\) is a coupling constant with dimensions frequency, \(a\) and \(a^\dagger\) are the annihilation and creation operators for a photon in the field mode, \(\sigma\) and \(\sigma^\dagger\) are the corresponding atomic ladder operators.
going into the many technical details (renormalisation, subtraction of classical energy shifts like Coulomb and polarisation self-interaction etc.).

For the multi-mode field, any one-photon state $|e; 1_{k\mu}\rangle$ is coupled via the nonresonant interaction to the ground state $|g; 0\rangle$, giving a coupling matrix element $\hbar g_{k\mu}$. Summing over all these modes, we find the energy shift

$$\delta E_{g0} = -\frac{1}{\hbar} \sum_{k\mu} \frac{\hbar^2 |g_{k\mu}|^2}{\omega_A + \omega_k}$$

$$= -\frac{1}{\hbar} \sum_{k\mu} \frac{E^2_k |d \cdot \varepsilon_{k\mu}|^2 |f_{k\mu}(x)|^2}{\omega_A + kc}$$

$$= -\frac{1}{\hbar} V \frac{V}{(2\pi)^3} \int d^3k \frac{\hbar kc}{2\varepsilon_0 V(\omega_A + kc)} \left( |d|^2 - |d \cdot \hat{k}|^2 \right) |f_k(x)|^2$$

We have introduced the mode functions $f_{k\mu}(x)$ (equal to $\exp(ik \cdot x)$ for a plane wave expansion) and, assuming that $|f_k(x)|^2$ is independent of $\mu$, performed the summation over the polarization unit vectors (as already seen a few times in the exercises). Good luck, the volume $V$ cancels with the factor $V^{-1/2}$ from the ‘field per photon’ $E_k$. The integration over the angles of $k$ gives:

$$\int \sin \theta \, d\theta \, d\varphi \left( |d|^2 - |d \cdot \hat{k}|^2 \right) = \frac{8\pi}{3} |d|^2.$$  \hspace{1cm} (3)

We are finally left with the radial integral

$$\delta E_{g0} = -\frac{8\pi}{6(2\pi)^3} \frac{|d|^2}{\varepsilon_0} \int_{0}^{\Lambda} \frac{k^3 \, dk}{\omega_A/c + k}$$

(wrong)  \hspace{1cm} (4)

This integral is obviously divergent in the limit $k \to \infty$, which is called an “ultraviolet catastrophe”. The integral is only finite if we introduce a cutoff wavenumber $\Lambda$. What order of magnitude can we reasonably give to $\Lambda$? Remember that our whole theory is based on the “long-wavelength approximation” (photon wavelength $2\pi/k$ much larger than atom size $\sim a_0$). For wave vectors $k \gg 1/a_0$ we therefore cannot trust our interaction Hamiltonian any more. Choosing the cutoff $\Lambda = 1/a_0$, we get a shift of the order of $d^2\Lambda^3/\varepsilon_0 = d^2/a_0^3 \sim e^2/\varepsilon_0 a_0$. This is a completely wrong result because it is of the order of the atomic binding energy!

To get the right result, one has to take into account self-energy terms that we did not explicitly write down in the Hamiltonian. These are infinite, too, but if they are evaluated with a similar cutoff and subtracted, one gets something which does not too badly diverge with the cutoff $\Lambda$:

$$\delta E_{g0} \approx \frac{1}{3\pi^2} \frac{|d|^2 \omega_0^3}{\varepsilon_0 c^3} \ln \left( \frac{\Lambda}{\omega_A/c} \right)$$  \hspace{1cm} (correct)  \hspace{1cm} (5)

Here, the correct value of the cutoff is given by … the Compton wavevector of the electron, $\Lambda = mc/\hbar$ (up to this wavevector is our nonrelativistic theory valid).
It is beyond the scope of this lecture to give a more detailed account of the Lamb shift calculation.

1.1.3 Van der Waals and Casimir-Polder forces

The previous calculation, as sick as it is, does give a result for the modification of the Lamb shift due to boundary conditions imposed on the electromagnetic field by macroscopic bodies. Let us focus on the simple case that our two-level atom is placed at a distance $z$ from a perfectly reflecting mirror. All we have to change in the calculation are the mode functions, and we shall use

$$f_{k\mu}(x) = \sqrt{2} \sin(kz) \exp[i(k_xx + k_yy)].$$

(We are actually cheating with the polarisation vectors to simplify things.) The factor $\sqrt{2}$ comes from the fact that we use a unitary transformation of the plane waves $e^{\pm ikz}$. We have to change the angular integration because now the $z$-axis plays a privileged role. We can expand the dipole moment in cartesian components and get ($\theta$ is now the angle between $k$ and the $z$-axis):

$$\int d\varphi |d \cdot \hat{k}|^2 = \int d\varphi |d_z \sin \theta \cos \varphi + d_y \sin \theta \sin \varphi + d_z \cos \theta|^2 = 2\pi \left( \frac{1}{2}d_z^2 \sin^2 \theta + \frac{1}{2}d_y^2 \sin^2 \theta + d_z^2 \cos^2 \theta \right)$$

Note that the integrals over the mixed terms involve $\cos \varphi$, $\sin \varphi$, or $\cos \varphi \sin \varphi$ whose average over one period vanishes. In terms of the components $d_\parallel = d_z$ and $d_\perp$ of the dipole parallel and perpendicular to the $z$-axis, we thus get

$$\delta E_{g0} = -\frac{1}{2(2\pi)^2\varepsilon_0} \int \frac{k^3dk \sin \theta d\theta}{\omega_a/c + k} \times \left( d_\parallel^2 \sin^2 \theta + d_\perp^2 (1 - \frac{1}{2} \sin^2 \theta) \right) \left( 1 - \cos(2kz \cos \theta) \right)$$

The ‘$1$’ in the last bracket is independent of the distance $z$ to the mirror — it will give the Lamb shift for an atom in free space. The second term with the $\cos$ gives the modification of the Lamb shift we are interested in. The $\theta$ integral gives (make the substitution $u = \cos \theta$ and differentiate with respect to $2kz$ to get the integrals with the additional factor $\cos^2 \theta$)

$$\int_0^\pi \sin \theta \, d\theta \, \cos(2kz \cos \theta) = \frac{2 \sin 2kz}{2kz}$$

$$\int_0^\pi \sin \theta \, d\theta \, \cos^2 \theta \cos(2kz \cos \theta) = \frac{2 \sin 2kz}{2kz} + \frac{4 \cos 2kz}{(2kz)^2} - \frac{4 \sin 2kz}{(2kz)^3}$$

$$\int_0^\pi \sin \theta \, d\theta \, \sin^2 \theta \cos(2kz \cos \theta) = -\frac{4 \cos 2kz}{(2kz)^2} + \frac{4 \sin 2kz}{(2kz)^3}$$

$^2$Alternative argument: normalise the volume integral of the squared mode function to $V$. 

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Apparently, we get an expression with different powers of \(1/z\).

Let us focus first on the **short-distance limit** and consider only the “most diverging” term \(\sim 1/z^3\). It involves the integral

\[
I_3(z) = \int_0^\infty \frac{dk \sin 2kz}{k_A + k}
\]

where we have put \(k_A = \omega_A/c\). We use a trick in the complex plane to perform the integration: write \(\sin 2kz\) as the imaginary part of \(e^{2ikz}\) and deform the integration path in the complex plane from the positive real axis to the positive imaginary axis. This works because the exponential \(e^{2ikz}\) vanishes at infinity, and the integrand has no pole in the upper left quadrant. Using the integration variable \(k = i\kappa\) on the imaginary axis, we find

\[
I_3(z) = \text{Im} \int_0^\infty \frac{dk e^{2ikz}}{k_A + k} = \text{Im} i \int_0^\infty \frac{d\kappa e^{-2\kappa z}}{k_A + i\kappa} = k_A \int_0^\infty \frac{d\kappa e^{-2\kappa z}}{k_A^2 + \kappa^2}
\]

We approximate this integral by noticing that it is the product of two decaying functions. The exponential decays on a scale given by \(1/z\), while the “Lorentzian” \(1/(k_A^2 + \kappa^2)\) decays on the scale \(k_A\). Now look at which scale is larger. The short distance regime is defined by the limit \(z \ll 1/k_A\): the distance is much smaller than the transition wavelength. Then the exponential decays much more slowly, and we can replace it by unity. This gives

\[
k_A z \ll 1 : \quad I_3(z) = k_A \int_0^\infty \frac{d\kappa}{k_A^2 + \kappa^2} = \arctan(\kappa/k_A) \bigg|_0^\infty = \frac{\pi}{2}
\]

The other inverse powers can be handled in a similar way and give sub-dominant contributions. We thus find the so-called van der Waals energy

\[
E_{vdW} = -\frac{1}{4\pi\varepsilon_0} \frac{d_\parallel^2 - \frac{1}{7}d_\perp^2}{8z^3} \quad (z \ll \lambda_A, \text{ wrong}).
\]

This is quite close to the correct result. The correct calculation with the proper handling of the polarisation vectors gives

\[
E_{vdW} = -\frac{1}{4\pi\varepsilon_0} \frac{d_\parallel^2 + \frac{1}{7}d_\perp^2}{8z^3} \quad (z \ll \lambda_A, \text{ correct}).
\]

which differs only in the sign of the \(d_\perp^2\) term. For realistic atoms, you get contributions from all excited states that are connected to the ground state (and from all their Zeeman sublevels).
In the **long-distance limit** \( k_A z \gg 1 \) (distance larger than transition wavelength), we can also evaluate the integral (7). Now the exponential has the fastest decay, and we can replace the lorentzian by a constant:

\[
k_A z \gg 1 : \quad I_3(z) = \frac{1}{k_A} \int_0^\infty d\kappa e^{-2\kappa z} = \frac{1}{2k_A z},
\]

and hence a result much smaller than in the short distance limit (because now \( k_A z \gg 1 \)). This occurs in fact for all terms we got. The final result is the famous Casimir-Polder energy:

\[
E_{\text{CP}} = -\frac{1}{4\pi\varepsilon_0} \frac{d^2}{4\pi k_A z^4} \quad (z \gg \lambda_A).
\]

where \( d^2 = d_\parallel^2 + d_\perp^2 \) (no distinction between the dipole orientations).

### 1.1.4 Summary

An atom in its ground state close to a planar surface feels an attractive potential that scales like \( 1/z^3 \) (van der Waals potential). This applies to distances much shorter than the wavelength \( \lambda_A \) of the strongest electric dipole transition starting from the ground state. The coefficient depends on the squared dipole moment \( d^2 \) of the atom, more precisely its expectation value in the ground state. At large distances \( z \gg \lambda_A \), a power law \( 1/z^4 \) is found (Casimir-Polder potential). The coefficient depends on \( d^2/\omega_A \), and this quantity is proportional to the atom’s static polarizability \( \alpha(0) \). More details on this calculation can be found, for example, in the textbook by Craig and Thirunamachandran [1] and the 1990 Les Houches lecture by Haroche [2].

For later reference, we quote here the result for the polarizability of the atomic ground state. This formula can be found by evaluating to lowest order in an applied electric field (frequency \( \omega \)) the average dipole induced moment.

\[
\alpha_{ij}(\omega) = \frac{2}{\hbar} \sum_e \frac{\omega_{eg} \langle g|d_i|e\rangle \langle e|d_j|g\rangle}{\omega_{eg}^2 - \omega^2 - 0i\omega}
\]

Here, the Bohr frequency between the ground state \( g \) and some excited state \( e \) is \( \omega_{eg} = (E_e - E_g)/\hbar \). The infinitesimal imaginary term in the denominator ensures causality: as a physical response function, the polarizability \( \alpha_{ij}(\omega) \) can only have poles in the lower half of the complex \( \omega \)-plane. Note that a number of different conventions for the units of the polarizability occur in the literature. In our notation, \( \alpha_{ij}(\omega)/\varepsilon_0 \) has the units of volume, and the average induced dipole moment is given by \( \langle d_i \rangle e^{-i\omega t} + \text{c.c.} = \alpha_{ij}(\omega) E_j(r) e^{-i\omega t} + \text{c.c.} \).
(Here and in the following, we use Einstein’s summation convention and drop the sum $\sum_j$.)

For the static polarizability, we get

$$\alpha_{ij}(0) = \sum_e \frac{2\langle g|d_i|e\rangle\langle e|d_j|g\rangle}{\hbar \omega_{eg}}.$$

If the ground state has spherical symmetry, this tensor is actually proportional to $\delta_{ij}$. (Note that in the hydrogen atom, this requires the summation over the three $p_x, p_y, p_z$ excited states.)

### 1.2 Role of field fluctuations

We now present an alternative viewpoint on the van der Waals force. Its advantage is that the role of field fluctuations is made explicit. Both vacuum and thermal fluctuations contribute at finite temperature. We develop a formalism that treats both in a unified way. At zero temperature, the standard van der Waals force is recovered. A thermal correction appears in the near field of a ‘hot’ surface.

The following section is adapted from the paper “Radiation forces on small particles in thermal near fields” by C. Henkel, K. Joulain, J.-P. Mulet, and J.-J. Greffet [J. Opt. A: Pure Appl. Opt. 4 (2002) S109].

#### 1.2.1 Radiation force

We consider a model system made from a dielectric half-space and a small (subwavelength) “test particle” in vacuum above. Both objects are possibly at finite temperature and radiate electromagnetic fields whose sources are thermal current fluctuations. Using the fluctuation electrodynamics framework of Lifshitz [3], the spectral density of these currents is related to the imaginary part of the dielectric function (for the half-space) or of the polarizability (for the particle).

We are interested in the force exerted by the radiation on the test particle. This force is actually both a time-average over the rapid fluctuations of the thermal field and an average over a statistical ensemble for the field. For particles with a subwavelength size, the force is given by [4]

$$F(r) = \sum_{i=x,y,z} \langle d_i(t) \nabla E_i(r, t) \rangle$$

where $d(t)$ is the dipole moment of the particle and $E(r, t)$ the total electric field at the particle’s position. The latter contains the fields generated by the thermal substrate...
and by the particle’s dipole moment, as well as the blackbody field in the vacuum half-space. The expression (11) combines both the Coulomb force (corresponding to the potential energy $-d \cdot E$) and the Lorentz force (involving the magnetic field), see [4]. As a simple derivation, we note that the force operator can be defined in terms the Heisenberg equation for the momentum operator

$$\hat{\mathbf{F}} = \hat{\mathbf{p}} = \frac{i}{\hbar} \{H, \mathbf{p}\} = -\nabla H_{\text{int}}$$

(12)

where we have used the fact that the atomic Hamiltonian is independent of the atomic center-of-mass position. Using the electric dipole interaction, one gets (11).

In our case, both the dipole moment and the electric field are fluctuating quantities. The force may therefore be written as a sum of two terms

$$\mathbf{F}(\mathbf{r}) = \langle d^{(\text{ind})}_i(t) \nabla E^{(\text{fl})}_i(\mathbf{r}, t) \rangle + \langle d^{(\text{fl})}_i(t) \nabla E^{(\text{ind})}_i(\mathbf{r}, t) \rangle$$

(13)

where the first describes the (spontaneous and thermal) fluctuations of the field that correlate with the corresponding induced dipole, while the second involves dipole fluctuations and the field they induce. There is no term involving fluctuations of both the dipole and the field: these are not correlated, since they originate from different physical systems. More precisely, to lowest order in perturbation theory, we can take the fluctuations in (13) to be those of the non-coupled atom+field system, these being obviously uncorrelated.

**1.2.2 Induced fluctuations**

The dipole induced by the field fluctuations is given by the particle’s polarizability:

$$d^{(\text{ind})}(\omega) = \alpha(\omega) \mathbf{E}(\mathbf{r}; \omega)$$

(14)

where we switched to frequency Fourier transforms and assumed an isotropic polarizability. Note also that $\mathbf{E}(\omega; \mathbf{r})$ is the total electric field at the dipole’s location. If we work at lowest order in the polarizability, we can identify this field with the fluctuating field $\mathbf{E}^{(\text{fl})}(\mathbf{r}; \omega)$ and ignore the scattering of this field by the particle. Otherwise, we could work with a “dressed” polarizability. Note however that the fluctuating field is not simply a collection of plane waves, but takes into account their scattering from the substrate.

The field induced by the dipole fluctuations is given by the electromagnetic Green tensor:

$$\mathbf{E}^{(\text{ind})}(\mathbf{x}; \omega) = \mathcal{G}(\mathbf{x}, \mathbf{r}; \omega) \cdot d(\omega),$$

(15)

where the variables $\mathbf{x}$ and $\mathbf{r}$ represent the observation and source point, respectively. To lowest order, we can identify the total dipole in (15) with its fluctuating component, as we did before for the field.
Finally, we express the operator product in terms of frequency Fourier transforms as
\[ \langle A(t) B(t) \rangle = \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} e^{i(\omega - \omega')t} \langle A^\dagger(\omega) B(\omega') \rangle \]  
(16)
where the frequency integrals run over both positive and negative frequencies. Without loss of generality, we have written the frequency integral for \( B(t) \) in terms of the conjugate operator \( B^\dagger[\omega] \). This is possible because in (13), both \( A(t) \) and \( B(t) \) are real (hermitian) operators.

1.2.3 Fluctuation spectra

**Dipole.** The dipole fluctuations of the particle are characterized by a spectral density given by the fluctuation–dissipation theorem. This assumes the particle to be at thermal equilibrium (temperature \( T_2/k_B \)) and gives \[ \langle d_i^\dagger(\omega)d_j(\omega') \rangle = 2\pi \delta(\omega - \omega')\delta_{ij} \frac{2\hbar}{e^{\hbar\omega/T_2} - 1} \text{Im} \alpha(\omega) \]  
(17)
Note that this expression applies to both positive and negative frequencies: for \( \omega > 0 \), we have \( (e^{\hbar\omega/T_2} - 1)^{-1} = \bar{n}(\omega/T_2) \), the average excitation number for Bose-Einstein statistics (vanishing at \( T = 0 \)). At negative frequencies, \( \omega < 0 \), we have \( (e^{\hbar\omega/T_2} - 1)^{-1} = -\bar{n}(\omega/T_2) + 1 \), and the minus sign is compensated by the symmetry relation \( \text{Im} \alpha_{ij}(\omega) = -\text{Im} \alpha_{ij}[-\omega] \) so that the total expression is positive again (as it should). In particular, at \( T_2 = 0 \), the dipole “fluctuates only at negative frequencies” which reflects the existence of the ground state (fluctuations can only connect to higher-lying states). We identify these fluctuations with spontaneous fluctuations. Thermal fluctuations are proportional to \( \bar{n} \) and are the same for positive and negative frequencies (as they should for classical noise spectra).

**Field.** For the field fluctuations, the fluctuation-dissipation theorem reads (field at temperature \( T_1 \)) \[ \langle E_i^\dagger(\mathbf{r}; \omega)E_j(\mathbf{r}'; \omega') \rangle = 2\pi \delta(\omega - \omega')\frac{2\hbar}{e^{\hbar\omega/T_1} - 1} \text{Im} G_{ij}(\mathbf{r}, \mathbf{r}'; \omega) \]  
(18)
where the imaginary part of the Green tensor appears. This result is valid at equilibrium (field and source at the same temperature). For a generalization to non-equilibrium, see below.

1.2.4 Resulting force

Collecting the different contributions to the force, we show that the “vacuum” fluctuations of both particle and substrate conspire to give the standard van der Waals–Casimir–Polder–London force. The thermal fluctuations give a correction that we evaluate in the limit of a particle at zero temperature.
Starting from the general expression \( (13) \), the force due to dipole fluctuations is (using the notation \( d_\omega = d\omega/2\pi \))

\[
\langle d_i^{(f)}(t) \nabla E_i^{(ind)}(r, t) \rangle = 2\hbar \int \frac{\tilde{d}_\omega}{e^{\hbar\omega/T_2} - 1} (\text{Im} \, \alpha(\omega)) \nabla_1 G_{ii}(r, r; \omega)
\]

(19)

where \( \nabla_1 \) is shorthand for the gradient with respect to the first position variable of the Green tensor.

The force due to field fluctuations is

\[
\langle d_i^{(ind)}(t) \nabla E_i^{(f)}(r, t) \rangle_{\text{vac}} = 2\hbar \int \tilde{d}_\omega \int \frac{\tilde{d}_\omega}{e^{\hbar\omega/T_1} - 1} \alpha^*(\omega) (\text{Im} \, \nabla_2 G_{ii}(r, r; \omega))
\]

(20)

We now argue that the Green tensor satisfies the symmetry relation

\[
\nabla_1 G_{ii}(r, r; \omega) = \nabla_2 G_{ii}(r, r; \omega).
\]

(21)

Very generally, the reciprocity theorem implies that the Green tensor is symmetric under combined exchange of the position arguments and vector indices \([5]\). For the particular case of the half-space, we have checked this explicitly. In this case, we also find that only the part involving the reflection from the interface remains under the derivative. This is because the (imaginary part of) the free space Green tensor depends only on \((r - r')^2\), due to isotropy, and has vanishing first derivative at \( r = r' \).

Using these results and specializing to the equilibrium case \( T_1 = T_2 = T \), we can combine (19), (20) to give the van der Waals force

\[
F_{vdW}(r) = 2\hbar \sum \text{Im} \frac{\tilde{d}_\omega}{e^{\hbar\omega/T} - 1} \alpha(\omega) \nabla_1 G_{ii}(r, r; \omega).
\]

(22)

You will find frequently in the literature an expression where the \( \omega \)-integral is transformed in the complex \( \omega \)-plane. One closes the integration path with a semicircle in the upper half plane. This circle does not contribute to the integral because \( \alpha(\omega) \) and \( G_{ij}(\omega) \), being physical response functions, decay to zero for \( |\omega| \to \infty \). In addition, they have no singularities in the upper half plane. The integral along the closed contour is thus determined by the poles of the Bose-Einstein factor at \( \omega = i\xi_n \equiv 2\pi nT/\hbar, \ n = 0, 1, 2 \ldots \) (‘Matsubara frequencies’). The pole \( n = 0 \) contributes with only one half of its residue because it lies on the original contour. One thus gets:

\[
F_{vdW}(r) = 2T \sum \text{Im} \frac{\tilde{d}_\omega}{e^{\hbar\omega/T} - 1} \alpha(i\xi_n) \nabla_1 G_{ii}(r, r; i\xi_n).
\]

(23)

(The prime reminds that \( n = 0 \) is counted with a factor \( 1/2 \).) We have dropped the ‘\( \text{Im} \)’ because the response functions are real at purely imaginary frequencies.
Zero temperature. In the limit of a particle at zero temperature, the Bose-Einstein distribution becomes a step function,

$$\lim_{T_1 \to 0} \frac{1}{e^{\hbar \omega/T_1} - 1} = H(-\omega),$$

showing that the integral runs only over negative frequencies. We thus find

$$F_{\text{vac}}(r) = 2\hbar \text{Im} \int_0^\infty \alpha(\omega) \nabla_1 G_{ii}(r, r; \omega),$$

where we have used the symmetry properties of $\alpha$ and $G_{ij}$. This result resembles up to a factor of 2 and a $-\nabla_1$ the expression for the van der Waals–Casimir–Polder–London energy given in [6]. The gradient occurs because we calculate the force, of course. To understand the factor 2, we note that when the force is calculated from the energy, both position dependences in $G_{ii}(r, r'; \omega)$ get differentiated. Close to a planar surface, both give the same contribution, since in the Weyl plane-wave expansion (see 1.4.1), the reflected part of the Green tensor is proportional to $e^{i\gamma(z+z')}$ where $\gamma$ is the normal component of the wave vector. In the planar geometry we consider here, the force is oriented perpendicular to the interface, of course.

We finally note that it is \textit{a priori} not clear that the light force derives from a potential because we are dealing with a dissipative system. At finite temperature and in equilibrium, the force is related to the energy change when the particle is displaced. This creates electromagnetic fields that do work on the polarization fluctuations, which is partly dissipated in the system. The corresponding potential energy is given by the free energy of the system. More details can be found in [7] and references therein. Here, at zero temperature and at lowest order in the polarizability, we do find a potential since $F$ can be written as a gradient. This need not be true at higher orders, however, because the combined state of atom and field develops correlations (the density matrix contains a term $\exp(d \cdot E(r)/T)$ involving the interaction Hamiltonian).

1.3 Fluctuation–dissipation theorem

We outline here a proof of the fluctuation–dissipation theorem for the electromagnetic field close to some arbitrary macroscopic object. The only requirement is that the object interacts in a linear way with the field and that thermal equilibrium prevails. This text is adapted from the review paper “Electromagnetic field fluctuations on the nanometer scale” by C. Henkel, submitted for publication in the Handbook of Theoretical and Computational Nanotechnology (2004).

The fluctuations of the electromagnetic fields can be characterized by statistical electrodynamics, which results from the application of equilibrium thermodynamics
and quantum theory to the macroscopic Maxwell equations [8]. We introduce in this
Section the basic definitions for the field fluctuation spectra and review how they can
be calculated. A key result in this context is the fluctuation dissipation theorem de-
rived by Callen and Welton [9] whose proof is sketched here. We conclude with some
remarks on how to handle non-equilibrium situations.

1.3.1 Basic definition

We shall assume that at thermodynamic equilibrium at temperature $T$, the field and
the solid medium can be described by a Gibbs ensemble: each state with energy $E$ is
weighted with the Boltzmann factor $\exp(-E/k_B T) \equiv e^{-\beta E}$. In the quantized
version of the theory, these states are stationary states: they are eigenstates with energy $E$
of the corresponding Hamilton operator $\hat{H}$. We shall work in the Heisenberg picture
where the field variables (called observables) evolve in time, while the state of the
system is fixed. The Gibbs ensemble is then characterized by the density operator

$$\hat{\rho}_{\text{eq}} = \frac{\exp(-\hat{H}/k_B T)}{\text{Tr} \exp(-\hat{H}/k_B T)}.$$ (26)

This is an operator on the Hilbert space of the system that can be represented by a
(infinite-dimensional) matrix, the density matrix. $\text{Tr} \exp(-\hat{H}/k_B T)$ is the trace of the
operator-valued Boltzmann factor, it is also called the partition function [10].

With respect to this equilibrium ensemble, we can define average values for the
observables of interest. This average combines the quantum expectation value in a
given stationary state with the corresponding statistical ensemble weights. The aver-
age electric field, for example is given by

$$\langle E(x, t) \rangle \equiv \text{Tr} \left[ E(x, t) \hat{\rho}_{\text{eq}} \right] = \text{Tr} \left[ \hat{\rho}_{\text{eq}} E(x, t) \right],$$ (27)

where we have made use of the cyclic permutation under the trace. The time-
dependence of the field is generated by the Hamilton operator, so that we have

$$\langle E(x, t) \rangle = \text{Tr} \left[ \exp(i\hat{H}t/\hbar) E(x) \exp(-i\hat{H}t/\hbar) \hat{\rho}_{\text{eq}} \right] = \text{Tr} \left[ E(x) \hat{\rho}_{\text{eq}} \right],$$ (28)

where $E(x)$ is the electric field operator at time zero and we have used that the Gibbs
density operator (26) is invariant under time evolution. The average can now be com-
puted in the Schrödinger picture and is found to vanish at equilibrium. In the classical
theory, this is because the phase of the field is uniformly distributed. In the quantum
theory, the stationary states for each mode of the field (labelled by $\kappa$) are eigenstates of
the photon number operator $a_\kappa^\dagger a_\kappa$. The field observable is a linear combination of the
annihilation and creation operators $a_\kappa^\dagger$ and $a_\kappa$ that lower or raise the photon number:
their quantum expectation values thus vanish in a photon number eigenstate. More
details can be found in Section 1.3.2 and in the textbooks by Loudon [11] and Mandel and Wolf [12].

The relevant information about the field fluctuations is thus encoded in the correlation function

\[ \langle E(x, t)E(x', t') \rangle \equiv \text{Tr} [E(x, t)E(x', t')\rho_{eq}] = \langle E(x, 0)E(x', t' - t) \rangle. \quad (29) \]

In the second step, we have shifted the time arguments using the fact that the time evolution commutes with the equilibrium density operator (26). As expected from stationarity, this correlation function only depends on the time difference \( \tau = t' - t \). In the limit \(|\tau| \to \infty\), one expects the fields \( E(x, t) \) and \( E(x', t') \) to decorrelate and the correlation function (29) to vanish. The time scale on which this happens gives the correlation or coherence time of the field.

The spectrum of the field fluctuations can be defined by the Fourier expansion of the correlation function

\[ \langle E(x, t)E(x', t') \rangle = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega(t' - t)} \mathcal{E}(x, x'; \omega). \quad (30) \]

This relation is also known as the Wiener-Khintchine theorem [12]. The spectrum is actually a tensor, the cross-spectral density tensor. For \( x = x' \), its components specify the local polarization state of the field. As a function of \( x - x' \), it characterizes the field’s spatial coherence, i.e., the contrast of interference fringes in a double-slit experiment with slits placed by \( x \) and \( x' \), see, e.g., the textbooks by Mandel and Wolf [12] and by Goodman [13]. As a function of the frequency \( \omega \), the spectrum specifies the strength of the field fluctuations. This can be seen from the equivalent relation for the Fourier transforms of the field

\[ \langle E(x, -\omega)E(x', \omega') \rangle = 2\pi \delta(\omega - \omega') \mathcal{E}(x, x'; \omega) = \langle (E(x, \omega))^\dagger E(x', \omega) \rangle. \quad (31) \]

In the last step, we have made use of the reality of the electric field that leads to identity \( [E(x, \omega)]^\dagger = E(x, -\omega) \) for real \( \omega \). This way of writing also shows that the diagonal elements of \( \mathcal{E}(x, x; \omega) \) are positive. More generally, \( 0 \leq u^* \cdot \mathcal{E}(x, x; \omega) \cdot u \) for any complex vector \( u \). We note that the Fourier transforms of the fields strictly speaking do not exist as ordinary functions. The Fourier calculus nevertheless applies symbolically for the corresponding operator-valued distributions.

The fluctuation spectrum of the electric field plays a key role for spontaneous and stimulated decay on the electric dipole transitions of an atom or molecule. The corresponding spectrum for the magnetic field characterizes the perturbation the field exerts on an atomic magnetic moment or spin. This is discussed in detail in Section 2.

\[ ^3 \text{Boldface vectors placed near each other mean a tensor product, often written } \otimes. \text{ Tensors are written in calligraphic letters like } \mathcal{E} \text{ or } \mathcal{H}. \]
1.3.2 Blackbody fluctuations

Let us illustrate the correlation function introduced above with the example of the blackbody radiation field in free space. The electric field operator can in that case be expanded in plane wave modes \[11, 12\]

\[
E(x, t) = \sum_\kappa \sqrt{\frac{\hbar \omega(k)}{2\pi V}} [a_\kappa(t) \varepsilon \exp(ik \cdot x) + \text{H.C.}],
\]

(32)

where the mode label \(\kappa = (k, \varepsilon)\) combines the wave vector \(k\) and the polarization vector \(\varepsilon \perp k\), and \(V\) is the quantization volume. We assume periodic boundary conditions so that the allowed wave vectors are discrete. The mode frequency is given by \(\omega(k) = ck = c\sqrt{k^2}\). ‘H.C.’ denotes the hermitean conjugate operator so that the electric field is globally hermitean. In the absence of any sources, the annihilation and creation operators evolve according to

\[
a_\kappa(t) = a_\kappa \exp[-i\omega(k)t], \quad a_\kappa^\dagger(t) = a_\kappa^\dagger \exp[i\omega(k)t].
\]

(33)

The Schrödinger operators \(a_\kappa\) and \(a_\kappa^\dagger\) satisfy the bosonic commutation relations

\[
[a_\kappa, a_\kappa^\dagger] = a_\kappa a_\kappa^\dagger - a_\kappa^\dagger a_\kappa = \delta_{\kappa, \kappa'} \equiv \delta_{k, k'}\delta_{\varepsilon, \varepsilon'}.
\]

(34)

The equilibrium expectation value of products of the mode operators decorrelates for different modes because the density operator factorizes into a product over all modes. Therefore, the expectation value \(\langle a_\kappa^\dagger a_\kappa\rangle\) vanishes for \(\kappa \neq \kappa'\).

For a given mode \(\kappa\), one gets from the Gibbs ensemble the Bose-Einstein occupation number (with \(\beta \equiv 1/(k_B T)\))

\[
\langle a_\kappa^\dagger a_\kappa \rangle = \bar{n}[\omega(k)] = \frac{1}{e^{\beta \hbar \omega(k)} - 1},
\]

(35)

\[
\langle a_\kappa a_\kappa^\dagger \rangle = 1 + \bar{n}[\omega(k)] = \frac{1}{1 - e^{-\beta \hbar \omega(k)}},
\]

(36)

while the products \(a_\kappa a_\kappa\) and \(a_\kappa^\dagger a_\kappa^\dagger\) have zero average. To prove Eq. (35), we evaluate the trace in the eigenbasis \(|n_\kappa\rangle\) of the photon number operator \(a_\kappa^\dagger a_\kappa\) for the given mode. The energy eigenvalue of \(|n_\kappa\rangle\) is \(\hbar \omega(k)(n_\kappa + \frac{1}{2})\), and the summation over the Boltzmann weights gives

\[
\langle a_\kappa^\dagger a_\kappa \rangle = \frac{\sum_{n_\kappa=0}^\infty n_\kappa e^{-\beta \hbar \omega(k)(n_\kappa + \frac{1}{2})}}{\sum_{n_\kappa=0}^\infty e^{-\beta \hbar \omega(k)(n_\kappa + \frac{1}{2})}}
\]

\[
= -\frac{\partial}{\partial \xi} \log \left( \sum_{n_\kappa=0}^\infty e^{-\xi n_\kappa} \right) \bigg|_{\xi = \beta \hbar \omega(k)} = \frac{\partial}{\partial \xi} \log \left( 1 - e^{-\xi} \right) \bigg|_{\xi = \beta \hbar \omega(k)}
\]

\[
= \frac{1}{e^{\beta \hbar \omega(k)} - 1}.
\]

(37)
Using these informations, a straightforward calculation in the continuum limit, \( \sum_k \rightarrow V \int d^3k/(2\pi)^3 \), leads to

\[
E(x, x + r; \omega) = \bar{\hbar}\omega \frac{3}{2} \bar{n}(\omega)(\bar{n}(\omega) + \frac{1}{2}) = 2\pi \text{DOS}(\omega) \frac{\hbar\omega}{2} \left( \bar{n}(\omega) + \frac{1}{2} \right),
\]

which only depends on the difference vector \( r = x' - x \), as expected. This expression is very similar to the Green tensor in free space which is not a coincidence, but a special case of the fluctuation-dissipation theorem introduced in Section 1.3.3.

In the limit \( r \rightarrow 0 \), one can check that \( E(x, x; \omega) \) is proportional to the unit tensor and positive. Taking the trace, one gets, up to a factor \( \varepsilon_0/2 \), the spectrum of the electric energy density \( u_e(\omega) \). Summing the contributions of positive and negative frequencies, the electric energy density is given by the Planck formula

\[
U_{bb, e}(\omega) = \int_0^\infty \frac{d\omega}{2\pi} u_{bb, e}(\omega),
\]

In the last expression, we have made use of the free space \( \text{DOS}(\omega) = \omega^2/\pi^2c^3 \). This result has an intuitive explanation: the electric energy density is the density of modes per unit volume, \( \text{DOS}(\omega)d\omega \), multiplied by one half of the average equilibrium energy \( \hbar\omega(\bar{n}(\omega) + \frac{1}{2}) \) of a harmonic oscillator (the other half contributes to the magnetic energy).

At zero temperature, the electric plus magnetic energy per mode is given by the ground state oscillator energy \( \hbar\omega/2 \), and this leads to a divergent integral in the UV. From this divergent zero-point energy, one can extract a finite, measurable energy difference, called the Casimir energy, when the mode functions are changed by the boundary conditions imposed by material structures. See the textbook by Mostepanenko and Trunov [14] for more details. The energy measured by a photodetector does not diverge because it is proportional to average of the photon number operator \( \langle a_k^\dagger a_k \rangle = \bar{n}(\omega(k)) \) [11, 12]. If the creation and annihilation operators are ordered in this way, the divergent contribution of the zero-point energy disappears. The black-body spectrum then shows an exponential decrease beyond the thermal wavelength \( \lambda_{th} = 2\pi\hbar c/(k_B T) \) (the Wien displacement law), and the frequency integral \[39\] becomes convergent.
1.3.3 Fluctuation-dissipation theorem

The previous example suggests that there is a relation between the field fluctuation spectrum and the Green function. With the previously introduced notation, we have

$$\mathcal{E}(x, x'; \omega) = \frac{2\hbar}{e^{\beta\hbar \omega} - 1} \text{Im} \mathcal{G}(x, x'; \omega),$$  \hspace{1cm} (41)

where the Green tensor is defined as the electric field radiated by a monochromatic point dipole,

$$E_{i}^{\text{(dip)}}(x; \omega) = \mathcal{G}_{ij}(x, r; \omega)d_{j}(\omega),$$  \hspace{1cm} (42)

and the fluctuation spectrum by Eq. (30). Eq. (41) is actually true under more general conditions and is known as a fluctuation-dissipation (FD) theorem \[9\]. It holds for linear systems and their fluctuations around the thermal equilibrium state. The dissipation is encoded in the imaginary part of the response function that characterizes the linear response of the system to an external perturbation. The FD theorem is of the form given here provided the Green tensor satisfies the symmetry condition specified in Eq. (21).

The FD theorem will be our basic tool to compute field fluctuation spectra in the near field of nanostructures. We give in this Section an introduction for linear systems and summarize a general proof in the context of statistical electrodynamics. A generalization to non-equilibrium situations is discussed in Section 1.3.4.

Johnson-Nyquist noise in metals. Consider a resistance at temperature $T$. One observes a thermal fluctuation of the current through the resistance, called Johnson noise, whose variance in a given bandwidth $\Delta f = \Delta \omega/(2\pi)$ is given by the Nyquist formula

$$\langle \delta I^2 \rangle_{\Delta \omega} = \Delta \omega \frac{4k_B T}{2\pi R(\omega)}. \hspace{1cm} (43)$$

We now show that this formula can be related to a fluctuation dissipation theorem for the current density $j(x)$ of the resistance. Consider first the $z$-component of the current density and a small volume element $\Delta V = \Delta z \Delta A$. From the current noise along the $z$-direction, one then has

$$\langle \delta j_z(x)^2 \rangle_{\Delta \omega} = \frac{\Delta \omega}{2\pi} \frac{4k_B T}{R(\omega)\Delta A^2} = \frac{\Delta \omega}{2\pi} \frac{4k_B T \sigma(\omega)}{\Delta V}, \hspace{1cm} (44)$$

where $\sigma(\omega) = \Delta z/(R(\omega)\Delta A)$ is the conductivity (the inverse of the specific resistance). In the low frequency range where the Nyquist formula is valid, the conductivity can be expressed via the dielectric function of the resistance, $\varepsilon_0 \varepsilon(\omega) = \varepsilon_0 + i\omega/\omega$. The result (44) can thus be obtained by averaging the following relation over the volume element

$$\langle \delta j(x)\delta j(x') \rangle_{\Delta \omega} = \frac{\Delta \omega}{2\pi} \frac{4k_B T \omega}{\text{Im} \varepsilon_0 \varepsilon(\omega)} \|\varepsilon(x; \omega)\| \delta(x - x').$$  \hspace{1cm} (45)
We have assumed that neighboring volume elements have uncorrelated current noise, hence the spatial delta function. We use here the convention that the current noise \((45)\) is given by the integral of the noise spectrum \(\mathcal{J}(x, x'; \omega)\) over intervals \(\Delta \omega/(2\pi)\) centered at positive and negative frequencies \(\pm \omega\). Since \(\omega \text{Im} \varepsilon(x; \omega)\) is an even function of \(\omega\), the noise spectrum is given by

\[
\mathcal{J}(x, x'; \omega) = 2k_B T \omega \mathbb{1} \text{Im} \varepsilon_0 \varepsilon(x; \omega) \delta(x - x').
\] (46)

This result has already the structure of the FD theorem \((41)\). Since the dielectric function gives the polarization induced by an electric field, a more natural formulation is in terms of the polarization noise spectrum (writing \(j(\omega) = -i\omega P(\omega)\))

\[
P(x, x'; \omega) = \frac{2k_B T}{\omega} \mathbb{1} \text{Im} \varepsilon_0 \varepsilon(x; \omega) \delta(x - x').
\] (47)

The temperature-dependent prefactor is the low-frequency limit of \(2h/(e^{\beta h\omega/k_B T} - 1)\) occurring in Eq. \((41)\). The spatial \(\delta\)-function applies to a local dielectric response. The generalization to a nonlocal medium is immediate: the fluctuations are then correlated on some characteristic scale, typically the mean free path.

We thus find that the strength of the thermal Johnson noise at a given frequency in an absorbing material is related to the amount of dissipation, as encoded in the imaginary part \(\text{Im} \varepsilon(\omega)\). This permits to characterize the thermal polarization and magnetization fluctuations that appear in the macroscopic Maxwell equations. The noise spectrum of the polarization noise \(P_{\parallel}(x; \omega)\) is given by the Johnson-Nyquist formula \((47)\), with the factor \(k_B T\) replaced by \(\hbar\omega/(e^{\beta \hbar \omega} - 1)\) to be valid at all frequencies. If the material is magnetic with a (local) permeability \(\mu(x; \omega)\), it contains magnetization fluctuations \(M_{\parallel}(x; \omega)\) with a spectrum

\[
\mathcal{M}(x, x; \omega) = -\frac{2h}{e^{\beta \hbar \omega} - 1} \text{Im} \frac{1}{\mu_0 \mu(x; \omega)} \delta(x - x').
\] (48)

The fluctuating material polarization radiates an electromagnetic field that, in thermodynamic equilibrium, compensates for the loss of electromagnetic energy inside the material. Only in this way is it possible to enforce the equipartition law of thermal equilibrium, every degree of freedom (here the polarization field) carrying an energy \(k_B T/2\). Consider the balance of electromagnetic energy for a system without external polarization sources. On the one hand, the mechanical work performed per unit time can be written as

\[
\omega \text{Im} (P_{\parallel}^\dagger(x; \omega) \cdot E(x; \omega'))
= 2\pi \omega \delta(\omega - \omega') \int d^3 x' P_{ij}(x, x'; \omega) \text{Im} G_{ij}(x, x'; \omega)
= 2\pi \delta(\omega - \omega') \frac{2h\omega}{e^{\beta \hbar \omega} - 1} \text{Im} \varepsilon_0 \varepsilon(x; \omega) \text{Im} \text{Tr} \mathcal{G}(x, x; \omega).
\] (49)
We have taken into account that only the part of the field radiated by the polarization fluctuation is correlated with the latter and expressed that field in terms of the Green tensor (42). A similar result holds for the magnetic contribution. On the other hand, the average over the electric losses in the medium leads to the same expression

\[ \omega \Im \langle \varepsilon_0 \varepsilon(x; \omega) \rangle \langle E^\dagger(x; \omega) \cdot E(x; \omega') \rangle \]

\[ = 2\pi \delta(\omega - \omega') \Im \langle \varepsilon_0 \varepsilon(x; \omega) \rangle \frac{2\hbar \omega}{e^{\beta \hbar \omega} - 1} \Im \text{Tr} G(x, x; \omega) , \]

(50)

using the fluctuation-dissipation theorem (41). As a result, the energy the polarization emits into the field [Eq.(49)] is exactly compensated for by the field energy lost by absorption, Eq.(50). This also implies that the average Poynting vector \( \Re \langle E^\dagger \times H \rangle \) vanishes, since there is no net energy transfer between medium and field.

We shall see that in the quantized theory, the polarization fluctuations of the material also contribute to the quantum fluctuations of the field. Otherwise, the dissipation present in the macroscopic Maxwell equations would force the field operators to decay to zero, including their commutators. These are preserved due to the quantum fluctuations of the material polarization. This picture suggests as well the existence of an FD theorem: the material loss that forces the fields to decay must be balanced by the fluctuations inside the material.

**Properties of quantum field fluctuations.** Before giving a general proof of the FD theorem (41), let us summarize some of the properties it implies for the equilibrium fluctuations of quantized fields.

The FD theorem allows to compute the quantum and thermal fluctuations of the electromagnetic field once the Green tensor is known. This quantity can be computed by solving the macroscopic Maxwell equations with point-like dipole sources. As long as the medium responds linearly to the field, the classical version of the theory is sufficient, quantum and thermal fluctuations are handled self-consistently using the theorem.

The noise spectrum of a quantized field is not symmetric. It is proportional to the Bose-Einstein occupation number \( n(\omega) \) for positive frequencies and decays to zero for \( \hbar \omega \gg k_B T \). At negative frequencies, one finds, given that \( \Im G(\omega) \) is an odd function, that the spectrum is proportional to \( 1 + n(|\omega|) \). The zero-point fluctuations appear here. The asymmetric frequency spectrum of zero-point or vacuum fluctuations can be understood qualitatively by noting that in the ground state, a system can only fluctuate via a virtual transition towards a state with higher energy. The corresponding Bohr frequencies are all positive. (That this leads to a spectral weight at negative \( \omega \) is related to our – conventional – choice of the exponential factor in the noise spectrum (30).) In the high-temperature limit or, equivalently, for classical systems, upward and downward transitions occur with equal probability, and the fluctuation spectrum is sym-
metric: \( \bar{n}(\omega) \approx \bar{n}(|\omega|) + 1 \approx k_B T / \hbar \omega \gg 1 \). For intermediate temperatures, we show below that the principle of detailed balance is satisfied, up- and downward transition rates differing by a factor \( e^{\beta \hbar \omega} \).

At positive frequencies, Eq. (30) shows that the spectrum \( E(x, x'; \omega) \) picks out that part \( E^{(+)}(x', t') \) of the electric field operator that evolves like \( e^{-i \omega t'} \). By analogy to time-dependent wave functions in quantum mechanics, this part is called the positive frequency part of the field. In the mode expansion (32), it corresponds to the sum over the annihilation operators \( a_\kappa \) [see also Eq. (33)]. Similarly, only the negative frequency part \( E^{(-)}(x, t) = [E^{(+)}(x, t)]^\dagger \) of the field operator contributes in the first factor. It follows that in the vacuum state, the expectation value

\[
\text{Tr} \left[ E^{(-)}(x, t) E^{(+)}(x', t') \hat{\rho}_{\text{vac}} \right] = 0
\]

vanishes since the annihilation operators, by definition, give zero when acting on the vacuum state. This operator order (annihilation operators acting first) is usually called ‘normal’ order. A typical example is the intensity measured by a photodetector [11, 12]. A nonzero vacuum expectation value occurs with the reverse operator order (creation operators acting first). This anti-normal order is picked out for negative frequencies in the fluctuation spectrum \( \mathcal{E}(x, x'; \omega) \). It gives nonzero results even in the vacuum state (at zero temperature), as we have seen in Eq. (36) and in the FD theorem (41).

**Proof of the FD theorem with linear response theory.** As mentioned previously, the macroscopic Maxwell equations in an absorbing medium have to be supplemented by material fluctuations in order to be consistent with thermodynamics and quantum theory. We thus split the polarization and magnetization operators into

\[
P(x, t) \rightarrow P^\text{fl}(x, t) + P^\text{ext}(x, t)
\]

\[
M(x, t) \rightarrow M^\text{fl}(x, t) + M^\text{ext}(x, t)
\]

(52)

where the terms with the subscript ‘fl’ describe the fluctuations in the material and the ‘ext’ all other sources like the dipole moments of atoms or molecules. In thermal equilibrium, the fluctuations average to zero, as we found after Eq. (28). In the following, more explicit information about the polarization noise is not needed. We shall assume that a Hamilton operator \( H \) exists that generates the macroscopic Maxwell equations as the Heisenberg equations of motion for the electric and magnetic field operators. (We are actually adopting a quantum Langevin picture, see Mandel and Wolf [12] and Gardiner [15].) A similar demonstration has been given by Wylie and Sipe [6].

The field fluctuation spectrum, from Eq. (50), is given by the expectation value

\[
\mathcal{E}(x, x' ; \omega) = \int_{-\infty}^{+\infty} d\tau e^{i \omega \tau} \langle E(x, 0) E(x', \tau) \rangle.
\]

(53)
We assume thermal equilibrium without external sources and have used the station-
arity of the correlation function. We now connect this spectrum to the linear response
of the field to an external dipole oscillator, following Calle n and Welton [9].

The solution for the electric field operator in the presence of a polarization source
can be represented in terms of the Green tensor in the quantum theory as well because
the substitution (52) preserves the linearity of the macroscopic Maxwell equations. We
thus get the field due to an operator-valued source, plus a term describing the free
evolution of the field

\[
E(x, t) = E_{\text{free}}(x, t) + \int \frac{d\omega}{2\pi} e^{-i\omega t} \int d^3 x' G(x, x'; \omega) \cdot \left[ P_\parallel(x'; \omega) + P_{\text{ext}}(x'; \omega) \right].
\]

There is a similar contribution from the magnetization that we do not need for the
present discussion. In equilibrium, the free field operator has zero average, and we
get the expectation value

\[
\langle E(x, t) \rangle = \int \frac{d\omega}{2\pi} e^{-i\omega t} \int d^3 x' G(x, x'; \omega) \cdot \langle P_{\text{ext}}(x'; \omega) \rangle.
\]

The Green tensor can thus be identified with the linear response of the average field
to a classical external polarization source (where \( P_{\text{ext}}(x'; \omega) \) is c-number valued).

The linear response of the field can also be calculated directly from the Heisenberg
equations. This provides us with an alternative expression for the Green tensor where
equilibrium correlations will become apparent. For simplicity, we focus in the follow-
ing on the response to an electric point dipole at the position \( x' \). The coupling of the
field to the dipole is described by adding to the Hamiltonian the term

\[
H_{\text{int}}(t) = -d(t) \cdot E(x', t),
\]

and the Heisenberg equation reads

\[
\frac{d}{dt} E(x, t) = -\frac{i}{\hbar} \left[ E(x, t), \hat{H} \right] + \frac{i}{\hbar} \left[ E(x, t), E_j(x', t) \right] d_j(t),
\]

where summation over \( j \) is understood in the last term. The first term generates the
free evolution of the field. Solving to first order in \( d \) and taking the average, we
identify the field response function in the time domain as

\[
\chi_{ij}(x, x', t - \tau) = \left\{ \begin{array}{ll}
\frac{i}{\hbar} \langle [E_i(x, t), E_j(x', t - \tau)] \rangle & \text{for } \tau \geq 0, \\
0 & \text{for } \tau < 0,
\end{array} \right.
\]

(59)
where the time dependence of the field operators is that of the evolution under $\hat{H}$. The response function is thus itself a correlation function of the field. Due to the stationarity of equilibrium, Eq. (59) does not depend on $t$. It can be checked directly that $\chi_{ij}(x, x', \tau)$ is real as in the classical theory. Taking the Fourier transform of $\chi_{ij}$, we thus get an expression for the Green tensor in terms of a field correlation spectrum

$$G_{ij}(x, x'; \omega) = \frac{1}{\hbar} \int_{0}^{+\infty} d\tau e^{i\omega\tau} \langle [E_i(x, \tau), E_j(x', 0)] \rangle. \quad (60)$$

By causality, the time integral is running over one half of the real axis only. We can make an integral over all $\tau$ appear, as it occurs in the fluctuation spectrum (53), by forming the combination

$$\frac{1}{2i} \{G_{ji}(x', x; \omega) - [G_{ij}(x, x'; \omega)]^*\} = -\frac{1}{2\hbar} \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} \langle [E_i(x, 0), E_j(x', \tau)] \rangle. \quad (61)$$

The following relation allows to permute operators occurring in equilibrium correlation functions:

$$\int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} \langle A(\tau)B(0) \rangle = e^{\beta \hbar \omega} \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} \langle B(0)A(\tau) \rangle. \quad (62)$$

In the classical theory, $\hbar = 0$ and operator ordering is irrelevant. Using this identity in the second term of the commutator in Eq. (61), we find the FD theorem:

$$E_{ij}(x', x; \omega) = \frac{2\hbar}{e^{\beta \hbar \omega} - 1} \frac{G_{ji}(x', x; \omega) - [G_{ij}(x, x'; \omega)]^*}{2i}. \quad (63)$$

The form (41) is recovered when the Green tensor satisfies the symmetry relation (21). This requires the additional assumption that permittivity and permeability are symmetric, an assumption that we shall make in this contribution.

Eq. (62) can be proved using the Gibbs density operator (26) and the solution for the Heisenberg operator $A(\tau)$ [see also Eq. (28):]

$$e^{i\omega \tau} \langle A(\tau)B(0) \rangle = e^{i\omega \tau} \frac{\text{Tr} \left[ \exp(i\hat{H}\tau/\hbar)A \exp(-i\hat{H}\tau/\hbar)B \exp(-\beta\hat{H}) \right]}{\text{Tr} \exp(-\beta\hat{H})}. \quad (64)$$

One shifts the integration path in the complex $\tau$-plane to the line $-\infty - i\hbar \beta \ldots +\infty - i\hbar \beta$ and assumes that for $|\tau| \to \infty$, the correlation function vanishes (otherwise this limiting value can be subtracted). Along the shifted path, Eq. (64) becomes

$$e^{\beta \hbar \omega} e^{i\omega \tau} \frac{\text{Tr} \left[ \exp(\beta\hat{H}) \exp(i\hat{H}\tau/\hbar)A \exp(-i\hat{H}\tau/\hbar) \exp(-\beta\hat{H})B \exp(-\beta\hat{H}) \right]}{\text{Tr} \exp(-\beta\hat{H})}.$$
\begin{align*}
= e^{\beta \hbar \omega} e^{i \omega \tau} \frac{\Tr \left[ B \exp(i \hat{H} \tau / \hbar) A \exp(-i \hat{H} \tau / \hbar) \exp(-\beta \hat{H}) \right]}{\Tr \exp(-\beta \hat{H})} \\
= e^{\beta \hbar \omega} e^{i \omega \tau} \langle B(0) A(\tau) \rangle,
\end{align*}

using cyclic permutation under the trace. The \( \tau \)-integral now yields the right hand side of Eq. (62).

### 1.3.4 Non-equilibrium situations

A typical non-equilibrium situation that occurs in physics on the nanometer scale is a temperature gradient inside a nanostructure. In thermal scanning probe microscopy, to quote another example, structures are held at different temperatures, being in contact with different reservoirs. These kind of settings can be described by a slight generalization of the present theory provided one assumes that each volume element of the solid structure is locally in thermal equilibrium at the temperature \( T(x) \). In this case, we can write down the fluctuation dissipation theorem for the thermal polarization field, by generalizing Eq. (47),

\begin{equation}
P(x, x'; \omega) = \frac{2 \hbar \Im \varepsilon_0 \varepsilon(x; \omega)}{\exp[\hbar \omega / k_B T(x)] - 1} \delta(x - x').
\end{equation}

We have assumed a local dielectric response for simplicity. The corresponding field fluctuation spectrum can be computed from the field operator (54) where the freely evolving field (with material damping, but without material fluctuations) and the Green tensor appear. Without external sources, one gets

\begin{equation}
\mathcal{E}_{ij}(x, x'; \omega) = \mathcal{E}_{ij}^{(\text{free})}(x, x'; \omega)
\end{equation}

\begin{equation}
+ \int_V d^3 r \left[ G_{ik}(x, r; \omega) \right]^* G_{jk}(x'; r; \omega) \frac{2 \hbar \Im \varepsilon_0 \varepsilon(r; \omega)}{\exp[\hbar \omega / k_B T(r)] - 1}.
\end{equation}

See Henry and Kazarinov for a similar approach [16]. The first term is nonzero for a bounded material surrounded by a non-absorbing dielectric (like free space) and describes the photons incident from infinity towards the observation points \( x, x' \). It accounts for all of the field fluctuations when there is no material absorption at all. If the field in the surrounding medium as assumed to be at zero temperature (like in the visible frequency range), this term is zero for \( \omega > 0 \). Even at finite temperature, however, this term is typically negligible at sub-wavelength distances from an absorbing structure. Under these conditions, the second one dominates i.e., the radiation due to the polarization noise (66). We summarize explicit examples above planar substrates in the next Section.
**Example: thermal van der Waals force.** Consider a planar, dielectric substrate at temperature $T_1/k_B > 0$, with the empty half-space above at zero temperature. This describes a thermal source surrounded by a vacuum chamber with absorbing walls at zero temperature [16]. (We neglect, of course, the heating of the walls due to the radiation from the substrate.) This model is the idealization of a situation where the dielectric is heated to a temperature higher than its surroundings.

The fluctuations of the electromagnetic field now have two contributions: a first one coming from the thermal currents in the substrate, and a second one coming from the vacuum fluctuations in the empty half-space. Written schematically,

$$
\langle E_i(r; \omega) E_j^\dagger(r'; \omega') \rangle = 2\pi \delta(\omega - \omega') \left\{ W_{ij}[\omega; T_1; r, r'] + V_{ij}[\omega; T = 0; r, r'] \right\} . \quad (68)
$$

There is no cross term because the two sources are not correlated. The spectrum $W_{ij}$ describes the radiation of the substrate and is computed using the Lifshitz model: it is the radiation produced by thermal current fluctuations inside the substrate. The spectrum $V_{ij}$ describes the vacuum field in the empty half-space. It may be calculated à la Lifshitz by allowing for a nonzero imaginary part into the vacuum dielectric constant that is put to zero in the final result [16, 17]. Alternatively, one can perform an explicit field quantization in the half-space [18] and retain only the modes incident from the vacuum side. The result is the same in both cases, of course.

The contributions in (68) can be combined in the following way to recover the equilibrium situation at $T_1 = 0$. We recall that for $\omega < 0$, the substrate field spectrum is proportional to $1 + \bar{n}(|\omega|/T_1)$, while the vacuum spectrum is proportional to $1 + 0 = 1$. Similarly, for positive frequencies, we have $W_{ij}(\omega) \propto \bar{n}(\omega/T_1)$, and $V_{ij} = 0$. Schematically, we may write

$$
W_{ij}[\omega; T_1; r, r'] = W_{ij}[\omega; T = 0; r, r'] + \bar{n}(|\omega|/T_1) W_{ij}[|\omega|; T = 0; r, r'] \quad (69)
$$

where the second term vanishes at zero temperature and is even in $\omega$. Those terms in (68) that survive at $T_1 = 0$ combine to give the zero temperature fluctuation-dissipation theorem.

The radiation emitted by the substrate (the second term in (69)) gives the explicitly temperature-dependent radiation. Note that this term is not the imaginary part of the Green tensor because we are not dealing with an equilibrium situation. Its behaviour as a function of frequency and the interpretation of the corresponding atom-surface force is given in [19].

### 1.4 Example: planar surface

In this section, we calculate the properties of the electromagnetic field close to a planar surface. The fluctuation-dissipation theorem is used, and a plane
wave expansion of the Green tensors for the electric and magnetic fields is worked out. Power law asymptotics are determined. This text is adapted from the habilitation thesis “Coherence theory of atomic de Broglie waves and electromagnetic near fields” (C. Henkel, Universität Potsdam, April 2004).

1.4.1 Electric and magnetic Green tensors

Consider a nonmagnetic solid with (relative) permittivity $\varepsilon$ and permeability $\mu = 1$ that fills the half-space $z \leq 0$. We shall be interested in the fluctuation spectrum of the electromagnetic field in the vacuum half-space, in particular for sub-wavelength distances $0 < z < \lambda \equiv 2\pi c/\omega$. Up to hundreds of nanometers from the surface, this regime is relevant even at optical frequencies.

For the Green tensor $G(x, x'; \omega)$, we can make the ansatz, provided both $x$ and $x'$ are located outside the solid,

$$G(x, x'; \omega) = G^{(\text{vac}))(x, x'; \omega) + G^{(\text{refl}))(x, x'; \omega)}$$  \(70\)

where $G^{(\text{vac})}$ is the vacuum Green tensor. $G^{(\text{refl})}$ describes the electric field reflected from the solid and is determined from the boundary conditions for the electric and magnetic fields at $z = 0$. The decomposition (70) is convenient to compute the field fluctuation spectra via the FD theorem (41) because it exhibits clearly the additional contribution due to the scattering from the surface [6, 5]. This statement remains true for scatterers of arbitrary shape, with a more complicated expression for the reflected or scattered field, of course.

Above a planar solid, the so-called Weyl expansion or angular spectrum representation provides a natural plane-wave basis for the incident and reflected fields, see the textbook by Nieto-Vesperinas [20]. The $xy$-plane naturally plays a distinguished role here. Introducing two-dimensional in-plane wave vectors $Q = (q_x, q_y)$, we shall use the notation

$$q(\pm) = Q \pm nq_z.$$

where $n$ is the unit normal. One then has the following Fourier expansion for the reflected Green tensor [6]

$$z, z' > 0: \quad G^{(\text{refl}}(x, x'; \omega) = \frac{i\omega^2}{2\varepsilon_0 c^2} \int \frac{d^2Q}{(2\pi)^2} \frac{e^{iq(\pm) \cdot x - iq(\pm) \cdot x'}}{q_z} \sum_{\mu = s, p} r_{\mu} e_{\mu}(+) e_{\mu}(-),$$  \(72\)

where the integral runs over all in-plane wave vectors $Q$. The wave vectors for downward and upward waves (both propagating and evanescent) are given by $q(-)$ and $q(+)$, respectively. The disc $|Q| \leq \omega/c$ corresponds to propagating waves where

$$q_z = \sqrt{(\omega/c)^2 - Q^2}, \quad \text{Im} q_z \geq 0$$  \(73\)
is real, while $|Q| > \omega/c$ describes evanescent waves that decay or increase exponentially with distance. Evanescent waves are required in the Green tensor to describe correctly the near field of a point dipole. For the reflected field, they provide the dominant contribution at subwavelength distances from the solid. All elementary plane waves satisfy the vacuum dispersion relation $(q(\pm))^2 = (\omega/c)^2$. Their polarization vectors are given by

$$e_s(\pm) = \hat{Q} \times n,$$

$$e_p(\pm) = \frac{q(\pm) \times e_s}{\omega/c} = \pm \frac{\hat{Q} q_z - nQ}{\omega/c},$$  

(74)

where $\hat{Q}$ is the unit vector along $Q$. We have normalized the polarization vectors (74) such that $e_{\mu}^2(\pm) = 1$; note that no complex conjugation is involved, although the vectors are complex in general. The conventional polarizations $s$ and $p$ are also called TE and TM in the literature (TE = electric field transverse to the plane of incidence spanned by $n$ and $Q$).

The reflection from the solid mixes downward with upward waves and is characterized by the Fresnel reflection coefficients [21, 22]

$$r_s = \frac{q_z - \sqrt{\epsilon(\omega)(\omega/c)^2 - Q^2}}{q_z + \sqrt{\epsilon(\omega)(\omega/c)^2 - Q^2}},$$  

(75)

$$r_p = \frac{\sqrt{\epsilon(\omega)(\omega/c)^2 - Q^2} - \epsilon(\omega)q_z}{\sqrt{\epsilon(\omega)(\omega/c)^2 - Q^2} + \epsilon(\omega)q_z}$$  

(76)

Note that the permittivity of the solid only enters via the Fresnel coefficients. As long as the planar symmetry is not broken, Eq. (72) can also be used above a multilayer medium [23, 24]. Note that sign conventions differ for the Fresnel coefficients and polarization vectors; only the product of $r_{\mu}$ and the polarization vectors appearing under the sum in Eq. (72) has an unambiguous meaning.

We define the magnetic Green tensor by analogy to Eq. (42) as the magnetic induction field radiated by a point magnetic moment

$$B_i(x;\omega) = H_{ij}(x, x';\omega)\mu_j.$$  

(77)

From the Maxwell equations we find that in terms of its electric counterpart, the magnetic Green tensor in the vacuum above the solid is given by the double curl

$$H_{ij}(x, x';\omega) = \frac{1}{\omega^2} \epsilon_{ikl}\epsilon_{jmn} \frac{\partial}{\partial x_k} \frac{\partial}{\partial x_m} G_{ln}(x, x';\omega).$$  

(78)

For the free space Green tensor, this leads to an expression similar to the electric case. For the reflected field, as given by the Green tensor (72), we observe that the curl exchanges the polarization vectors (74) according to

$$q \times e_s = \frac{\omega}{c} e_p,$$

$$q \times e_p = -\frac{\omega}{c} e_s$$  

(79)
because \( q, e_s, \) and \( e_p \) form an orthogonal Dreibein. Hence, up to a factor \( 1/c^2 \), we obtain the magnetic field reflected from the solid by exchanging the reflection coefficients \( r_s \leftrightarrow r_p \) in Eq. (72).

1.4.2 Short distance expansions

To illustrate the behaviour of the field at short distances, we review here asymptotic expansions for the electric and magnetic Green tensors.

**Electric field.** As a first step, we show that in the near field, the reflected part (72) of the electric Green tensor takes a simple, electrostatic form. The integral over the wave vector \( Q \) involves the factor \( e^{i (q_z z + q_z' z')/(z + z') \gg \omega/c} \). Analyzing the integrand, we notice that it peaks around the cutoff value. We thus get the leading order asymptotics by using an expansion for \( Q, |q_z| \gg \omega/c \) under the integral.

Let us first assume the more stringent condition \( Q \gg |\sqrt{\varepsilon}| \omega/c \) which corresponds to a distance much shorter than the medium wavelength, \( z \ll \lambda/|\sqrt{\varepsilon}| \). The reflection coefficients and polarization vectors then behave like

\[
\begin{align*}
    r_s e_s(+) e_s(-) &\approx (\varepsilon - 1) \frac{\omega^2}{4Q^2 c^2} (n \times \hat{Q})(n \times \hat{Q}), \\
    r_p e_p(+) e_p(-) &\approx \frac{\varepsilon - 1}{\varepsilon + 1} \frac{Q^2 c^2}{\omega^2} (n - i\hat{Q})(n + i\hat{Q}),
\end{align*}
\]

where \( n \) is the surface normal. The polarizations behave very differently, the p-polarized part dominating for large \( Q \) by a factor \((Qc/\omega)^4\). The reflection coefficient \( r_p \) tends towards the electrostatic value \( r_{stat} = (\varepsilon - 1)/(\varepsilon + 1) \) and becomes independent of \( Q \). This means that the reflection from the surface is nondispersive and can be modeled in terms of image theory [21]: the reflected field corresponds to the well-known field of an image dipole \( \tilde{d} = (-d_x, -d_y, d_z)r_{stat} \) located at the position \( X' - z'n \) below the surface. Performing the integrals over \( Q \), we indeed find the short-distance asymptotics

\[
G^{(refl)}(X' + R, z, X', z'; \omega) \approx \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \frac{(R^2 + \tilde{z}^2)1 - 3R\tilde{R} + (\tilde{z}^2 - 2R^2)nn + 3\varepsilon(Rn - nR)}{4\pi\varepsilon_0 (R^2 + \tilde{z}^2)^{3/2}},
\]

where \( \tilde{z} = z + z' \) and \((R^2 + \tilde{z}^2)^{1/2}\) is the distance between the observation point and the image dipole. This expression depends on frequency only via the electrostatic reflection coefficient. Note also the broken isotropy of the correlation tensor where the coordinates parallel and perpendicular to the surface appear in non-equivalent ways. Nevertheless, the symmetry relation [21] is satisfied.
In a similar way, an asymptotic expression for distances larger than $\lambda/|\sqrt{\varepsilon}|$ can be worked out. This is particularly interesting above metallic surfaces where $\varepsilon \approx i\sigma/\varepsilon_0\omega$ can be very large. In this case, the expansion (82) is valid for $z \ll \delta_\omega$ where the skin depth
\[
\delta_\omega \equiv \sqrt{\frac{2\varepsilon_0c^2}{\sigma\omega}}
\] (83)
can be much smaller than the wavelength (typically, at frequencies below the infrared). For the complementary range $\delta_\omega \ll z$, one finds, repeating the analysis leading to the asymptotics (80), (81) (see [25])
\[
\text{Im} G(X, z, X', \omega) \approx \frac{\omega^2\delta_\omega}{32\pi\varepsilon_0c^2 z^2}.
\] (84)

For simplicity we give only the imaginary part of the tensor with coinciding positions. Note the different power law with distance $z$ and also the isotropic noise strength regarding the field polarization.

To summarize, the electric field fluctuation spectrum derived from the Green tensor (82) using the FD theorem (41) is
\[
E(x, x'; \omega) = \frac{\hbar(\omega\delta_\omega/e)^2}{16\pi\varepsilon_0(e^{\beta\hbar\omega} - 1)} \begin{cases} 
\frac{1 + \text{nn}}{z^3} & \text{for } z \ll \delta_\omega, \\
\frac{1}{\delta_\omega z^2} & \text{for } \delta_\omega \ll z \ll (\delta_\omega\lambda)^{1/2}, \\
\frac{16\omega}{3\varepsilon_0\delta_\omega^2} & \text{for } (\delta_\omega\lambda)^{1/2} \leq z.
\end{cases}
\] (85)

It is only at distances $z \geq (\delta_\omega\lambda)^{1/2}$ that the blackbody spectrum, originating from the free space contribution (third case in Eq. (85)), becomes the dominant contribution. Closer to the surface, the electric field fluctuations have a noise spectrum that can exceed the Planck formula by several orders of magnitude. Note also that the low frequency limit is given by a constant spectrum $\propto k_B T/(\sigma z^3)$. The electric field fluctuations thus behave like white noise on the nanometer scale.

**Magnetic field.** Analogous calculations give for the Green tensor of the magnetic field at distances below the skin depth, $z, z' \ll \delta_\omega$,
\[
H^{(\text{refl})}(X' + R, z, X', z'; \omega) \approx \frac{\omega^2\mu_0}{4\pi c^2} \left\{ \frac{\varepsilon(\omega) - 1}{4\tilde{\tau}(\tilde{\tau} + \tilde{z})} \left[ \tilde{\tau} \frac{1}{\tilde{\tau} + \tilde{z}} + \tilde{z} \frac{\text{nn}}{\tilde{\tau}} + (\text{nn} - \text{nn}) \right] \\
+ \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \frac{\tilde{\tau} + \tilde{z}}{\tilde{\tau}(\tilde{\tau} + \tilde{z})} \right\}.
\] (86)
where \( \tilde{r} = (R^2 + \tilde{z}^2)^{1/2} \). From the fluctuation-dissipation theorem, we get the fluctuation spectrum of the magnetic field. We give here also the regimes of larger distances

\[
B(x, x; \omega) = \frac{\hbar \mu_0}{8\pi \delta_\omega^2 (e^{\hbar \omega T} - 1)} \begin{cases} 
\frac{1 + \text{nn}}{z} & \text{for } z \ll \delta_\omega, \\
\frac{\delta_\omega^2 (1 + \text{nn})}{3z^4} & \text{for } \delta_\omega \ll z \ll (\delta_\omega \lambda^3)^{1/4}, \\
\frac{8\delta_\omega^2 \lambda^3}{3e^3} & \text{for } (\delta_\omega \lambda^3)^{1/4} \leq z.
\end{cases}
\]  

(87)

Note the different exponents for the power laws with distance compared to the electric field, and the larger cross-over distance to the blackbody radiation spectrum. The low-frequency limit of the magnetic noise spectrum is \( \propto \mu_0^2 k_B T \sigma / z \), it is frequency-independent as well. Similar expressions have been derived in [26, 25, 27].

### 1.4.3 Electromagnetic energy densities

Some of the results summarized above have been discussed by Joulain, Carminati, Mulet, and Greffet in a recent paper on the definition and measurement of the LDOS close to planar surfaces [28]. These authors analyze the spectrum of the electric and magnetic energy densities \( u_e(z; \omega), u_m(z; \omega) \) as a function of distance and point out that the definition of the LDOS should be taken with care given the non-equivalent role played by the electric and magnetic fields in the near field. To illustrate this, we plot in Figure 1 the ratio \( u_m(z; \omega) / u_e(z; \omega) \). Notice the strong dominance of the magnetic energy throughout the near field range up to \( z \sim \lambda \) for a metallic surface. The asymptotic formulas (85), (87) provide good agreement with a numerical calculation based on the exact plane wave expansion (72) for the electric Green functions and its magnetic equivalent.

For a dielectric surface with an essentially real permittivity, the near field energy is dominantly electric, as shown in Fig. 1 (right). This behavior is not covered by the asymptotics (85), (87) because the assumption \(|\varepsilon| \gg 1\) breaks down, but can be found from (82) and its magnetic counterpart. At distances comparable to the wavelength, oscillations appear for both metallic and dielectric surfaces, that correspond to the standing waves formed by the partial reflection of the field. In the far field regime \( z \gg \lambda \), the symmetry between electric and magnetic energy is restored, as expected from the Planck formula.

### 1.5 Discussion of the van der Waals force

#### 1.5.1 Short distance limit

The dynamic polarizability for an atomic ground state has been given in (10). A transition frequency \( \omega_{eg} \) provides a natural scale for the \( \omega \)-integral of the van
Figure 1: Ratio of magnetic to electric energy density vs. distance from a medium-filled half-space, normalized to the wavelength $\lambda$. Left panel: metal with $\varepsilon = 1 + 800i$ (skin depth $\delta = 0.008\lambda$). Right panel: dielectric ($\varepsilon = 2.3 + 0.1i$, $\delta > \lambda$). The dashed and dotted lines correspond to the asymptotic expansions (85), (87).

...nder Waals force. As a first estimate, we can assume that frequencies around the strongest electric dipole transition, $\omega \sim \omega_{eg}$ contribute most strongly to the integral. This allows to define the short distance limit: the distance is small compared to the corresponding (reduced) wavelength, $z \ll \lambda_{eg} \equiv c/\omega_{eg}$. Note that the same physical limit is achieved by neglecting retardation, $c \to \infty$, or focusing on low frequencies, $\omega \sim \omega_{eg} \to 0$.

Now, the low frequency (small distance) limit of the Green tensor is simply given by electrostatics. For a planar surface, the reflected field can be constructed in terms of an image dipole located below the surface at a symmetric point. From this construction, one finds a Green tensor

$$G_{ij}^{(sc)}(r, r'; \omega) = \frac{1}{4\pi\varepsilon_0} \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \frac{\delta_{ij} + \delta_{ix}\delta_{jz}}{(2z)^3},$$

as also outlined around Eq. (82). The van der Waals interaction energy is now given by

$$E_{vdW}(z) \approx -\frac{1}{2\pi\varepsilon_0(2z)^3} \sum_e \left( |\langle g|d|e\rangle|^2 + |\langle g|d_z|e\rangle|^2 \right) \times \text{Im} \int_0^{\infty} d\omega \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \frac{\omega_{eg}}{\omega_{eg}^2 - \omega^2 - 0i\omega}. \quad (89)$$

This expression is used to interpret high-resolution atomic spectra near surfaces, see the lecture by D. Bloch. Particularly interesting features occur when the atomic resonance, $\omega \sim \omega_{eg}$, gets close to a “surface resonance”, $\varepsilon(\omega) \sim -1$. If a model for the dielectric function valid at complex frequencies is known,
one can also evaluate the integral in (89) along the imaginary axis:

\[ \int_{0}^{\infty} \frac{d\xi}{2\pi} \frac{\varepsilon(i\xi) - 1}{\omega_{eg}} = \int_{0}^{\infty} \frac{d\xi}{2\pi} \frac{\varepsilon(i\xi) + 1}{\omega_{eg}^2 + \xi^2}. \]  

(90)

All quantities here are real and positive so that no real or imaginary part is needed any more.4

### 1.5.2 Large distance limit

At large distances, we have to use the full Green tensor. It can be written in the form

\[ G_{ij}^{(sc)}(r, r'; \omega) = \frac{i}{8\pi\varepsilon_0} \int_{0}^{\infty} K dK \frac{e^{2i\gamma z}}{\gamma} \left\{ \omega^2 \Delta_{ij} r_s(\varepsilon) + \left( K^2 \delta_{iz} \delta_{jz} - \gamma^2 \Delta_{ij} \right) r_p(\varepsilon) \right\} \]  

(91)

where \( \Delta_{ij} = \text{diag}(1, 1, 0) \) in a frame where the \( z \)-axis points normal to the surface. The distance occurs in the exponential

\[ \exp(2i\gamma z) = \exp(-2z\sqrt{K^2 - \omega^2/c^2}). \]  

(92)

One shifts the \( \omega \)-integration onto the imaginary axis and observes that in the limit \( z \to \infty \), only small values of \( K \) and \( \omega = i\xi \) contribute. We can thus expand the integrand for small \( K \) and \( \xi \) and evaluate the integral. We find to lowest order the static atomic polarizability \( \alpha_{ij}^{(\text{stat})} \). The combination \( \kappa = \sqrt{K^2 + \xi^2/c^2} \) is a good integration variable, and the integral gives the famous \( 1/z^4 \) power law of the “Casimir–Polder” interaction. The remaining integral can be written in terms of an angle \( \alpha \) (with \( \xi = \kappa \cos \alpha \)), and we get

\[ V_{CP}(z) = -\frac{3\hbar c \alpha_{ij}^{(\text{stat})}}{8\pi^2\varepsilon_0(2z)^4} \times \int_{0}^{\pi/2} \sin \alpha \left\{ -\cos^2 \alpha \Delta_{ij} r_s(\varepsilon^{\text{stat}}) + \left( 2\sin^2 \alpha \delta_{iz} \delta_{jz} + \Delta_{ij} \right) r_p(\varepsilon^{\text{stat}}) \right\}. \]  

(93)

The reflection coefficients are evaluated with the static dielectric constant, but depend in general on \( \alpha \), for example:

\[ r_s(\varepsilon^{\text{stat}}) = \frac{1 - \sqrt{\varepsilon^{\text{stat}} \cos^2 \alpha + \sin^2 \alpha}}{1 + \sqrt{\varepsilon^{\text{stat}} \cos^2 \alpha + \sin^2 \alpha}} \]  

(94)

4 A response function at \( \omega = i\xi \) corresponds to the response to a real-valued excitation that is exponentially switched on, \( \propto e^{\xi t} \). Since the physical response is a real (hermitean) variable, the response function is real as well.
For a perfect conductor and also for metals with a nonzero DC conductivity, \( \varepsilon_{\text{stat}} = i \infty \), and therefore \( r_s \equiv -1 \) and \( r_p \equiv +1 \). In that case, the \( \alpha \)-integral gives \( \frac{4}{3}\delta_{ij} \).

2 Transitions

In this second part of the lecture, we discuss transitions between different quantum states of a trapped atom that are induced by electromagnetic fluctuations. For atoms trapped close to surface, the relevant quantum states are: Zeeman or hyperfine sublevels that are trapped in potentials of different steepness (or not trapped at all), and center-of-mass eigenstates in the trapping potential. In the first case, transitions lead to trap loss or to the decoherence of Zeeman or hyperfine superposition states. In the second case, field fluctuations feed energy into the center-of-mass motion and give heating.

The transition rates can be computed, as a first approximation, with second-order perturbation theory, using Fermi’s Golden Rule. We shall find out that the rates are indeed small so that higher order corrections are usually not needed. We show in particular that the transition rate is a measure of the cross spectral density of the field fluctuations. Let us look first at the transition between different magnetic sublevels. The following section is adapted from the paper “Fundamental limits for coherent manipulation on atom chips” by C. Henkel, P. Krüger, R. Folman, and J. Schmiedmayer [Appl. Phys. B 76 (2003) 173].

2.1 Noise spectrum and spin flip rate

The coupling of the atomic magnetic moment to fluctuating magnetic fields gives rise to both spin flips and changes in the center-of-mass motion (scattering). The rate of these processes is given by Fermi’s Golden Rule. We recall here that it can be conveniently expressed in terms of the noise spectrum of the magnetic field fluctuations. (See [6] for a similar approach and Chap. IV of [29] for the derivation of a full master equation.)

If we write \(|i\rangle\) and \(|f\rangle\) for the atomic states before and after the transition, the transition rate is

\[
\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} \sum_{F,I} p(I) |\langle F, f | H_{\text{int}} | I, i \rangle|^2 \delta(E_F + E_f - E_I - E_i),
\]

where \(|I\rangle\) and \(|F\rangle\) are initial and final states for the field, the summation being an
average over the initial field states (with probabilities \( p(I) \)) and a trace over the final
field states. The interaction Hamiltonian is given by \( H_{\text{int}} = -\mathbf{\mu} \cdot \mathbf{B}(x) \).

Consider first the rate for spin flips. Since only a subset of magnetic sublevels
\(|m_i\rangle\) are weak field seekers, spin flips \(|m_i\rangle \rightarrow |m_f\rangle\) are responsible for trap loss. The
magnetic field is evaluated at the position \( r \) of the trap center. (An average over the
atomic position distribution would be more accurate.) We write the \( \delta \)-function for
energy conservation as a time integral over \( e^{i(E_i - E_f - \hbar \omega_{fi})t/\hbar} \) where \( \hbar \omega_{fi} = E_f - E_i \).
The exponential \( e^{i(E_i - E_f)t/\hbar} \) can be removed by introducing the field operators in the
Heisenberg picture
\[
\mathbf{B}(r, t) = e^{iH_0t/\hbar} \mathbf{B}(r) e^{-iH_0t/\hbar}
\] (96)
(here, \( H_0 \) is the free field Hamiltonian) and taking matrix elements of this operator
between the initial and final field states. This gives
\[
e^{i(E_i - E_f)t/\hbar} \langle I | \mathbf{B}(r) | F \rangle = \langle I | \mathbf{B}(r, t) | F \rangle.
\] (97)
The sum over the final states \(|F\rangle\) now reduces to a completeness relation and we get
(\( \alpha, \beta \) denote field components)
\[
2\pi \hbar \sum_{F,I} p(I) \langle I | B_\alpha(r) | F \rangle \langle F | B_\beta(r) | I \rangle \delta(E_f - E_i - \hbar \omega)
\]
\[
= \int dt e^{i\omega t} \sum_{I} p(I) \langle I | B_\alpha(r, t) | \beta(r, 0) | I \rangle
\]
\[
= B_{\alpha\beta}(r, r; \omega).
\] (98)
In the last line, we have defined the magnetic noise spectrum which is the Fourier
transform of the field’s autocorrelation function. The rate for spin flips can now be
written as
\[
\Gamma_{i \rightarrow f} = \frac{1}{\hbar^2} \sum_{\alpha, \beta=x,y,z} \langle m_i | \mu_\alpha | m_f \rangle \langle m_f | \mu_\beta | m_i \rangle B_{\alpha\beta}(r, r, -\omega_{fi}).
\] (99)
Since \( m_f \neq m_i \), the matrix elements of \( \mu_\alpha \) are only nonzero for directions perpen-
dicular to the magnetic field at the trap center. We also recover the selection rule
\( m_f - m_i = \pm 1 \) so that the relevant transition frequency is the Larmor frequency
\( \omega_{fi} = \omega_L \). The spin flip rate gives the order of magnitude of trap loss even if more
than one weak-field seeking Zeeman states, \( m_i = +2, +1 \), say, are trapped (possible
with many of the alkali atoms). This is because the matrix elements between adja-
cent sublevels do not significantly differ in magnitude so that the atoms reach the
non-trapped sublevel \( m_f = 0 \) after a time \( \sim 2/\Gamma_{+2 \rightarrow +1} \).

We finally note that as long as the behaviour of the ‘environment’ (the field) is ig-
nored in the description of the atom’s dynamics, the noise spectrum is the only quan-
tity needed to characterize the environment. It is also an experimentally measurable
quantity: for example, the rms magnetic noise $\langle B_x^2(r) \rangle^{1/2}$ measured by a spectrum analyzer in a given frequency band $\Delta \omega/2\pi$ around $\omega$ is $(2B_{xx}(r, r; \omega) \Delta \omega/2\pi)^{1/2}$, the factor 2 accounting for the sum over positive and negative frequencies. The atomic spin flip rate may be regarded as an alternative way to measure the noise spectrum. In order of magnitude, the magnetic moment is comparable to the Bohr magneton, $\mu_B$ ($\mu_B/2\pi\hbar = 1.4$ MHz/G), and we get

$$\Gamma_{i\to f}(r) \sim 0.01 s^{-1}(\mu/\mu_B) \frac{2B_{\alpha\beta}(r, r; \omega_L)}{pT^2/Hz}. \quad (100)$$

Note that current SQUID magnetometers are able to detect magnetic field noise even on the $10 fT/\sqrt{Hz}$ scale [27].

### 2.2 Magnetic near field noise

Eq. (99) clearly shows that we need the spectrum of the magnetic field fluctuations for an estimate of the spin flip transition rate. The fluctuation–dissipation theorem provides the spectrum in terms of the Green function $H_{ij}(x, x'; \omega)$ for the magnetic field,

$$B_{ij}(x, x'; \omega) = \frac{2\hbar}{e^{\hbar \omega/\Delta_{\omega} - 1}} \text{Im} H_{ij}(x, x'; \omega). \quad (101)$$

The regime typical for trapped atom experiments is sub-wavelength distances, where the magnetic Green tensor (remember: the field radiated by a point magnetic moment) is dominated by the part reflected or scattered from the surface. From the short-distance expansion (86), we find two regimes, depending on the relative magnitude of the distance compared to the skin depth inside the surface material.

**Very short distance, normal conductor.** The skin depth $\delta_\omega$ is large compared to the distance. As a scaling law for a normal metal,

$$\delta_\omega = 160 \mu m \left( \frac{\rho/\rho_{Cu}}{\omega/2\pi \text{ MHz}} \right)^{1/2}, \quad (102)$$

where $\rho$ is the specific resistance. The scaling of the spin flip rate is then

$$\Gamma_{i\to f} \propto \frac{T}{\rho z}, \quad (103)$$

This estimate applies to a half-space. For absolute numbers, see the lecture by J. Schmiedmayer. Note in particular that the flip rate is independent of the
Larmor frequency. This is due to a conspiracy between the “density of states” of the magnetic near field ($\propto \omega$) and the Bose-Einstein occupation number ($\propto 1/\omega$).

The estimate (103) can be extended to other geometries using the following argument. In this “very short distance” regime, the distance $z$ gives the depth of the material that contributes significantly to the magnetic noise outside the surface. This has been checked by an explicit calculation in [27] [30]. Any structure thicker than $z$ thus essentially behaves like a half-space. One gets a reduction of the magnetic noise spectrum for thinner films or wires, for example. Each dimension along which the metallic material becomes “finite” (characteristic length $a$ like thickness or wire radius) gives an additional factor $a/z$ for the noise spectrum and hence for the spin flip rate. It is likely that this explains the cross-over seen in the lifetime data vs. distance of J. Schmiedmayer’s group.

If one works in the short-distance regime, the optimal material choice is an insulator (large resistance $\rho$). For strong magnetic fields, permanently magnetized structures can be used. Alternatively, materials may exist whose conductivity is reasonably large in the DC range and sufficiently small in the kHz to MHz range that applies for the relevant transitions.

**Intermediate distance, very good conductor.** At larger distances or equivalently, smaller resistance, the skin depth ultimately becomes smaller than the distance. In this regime, a different power law is obtained. One gets a steeper scaling with distance,

$$\Gamma_{1\to f} \propto \frac{T}{\omega L} \frac{\rho^{1/2}}{z^4},$$

which is now also frequency dependent. This regime should also apply to superconducting substrates. Note that in the relevant frequency range, even a superconductor shows some finite resistance due to the normal electron fraction not bound into Cooper pairs.

In this regime, one can say that qualitatively, only the surface of the material produces magnetic field fluctuations. The power laws for different geometries therefore do not probably show the cross-over seen at short distance. The problem is currently under study. Estimates for magnetic noise above superconducting substrates are given in the review by J. A. Sidles [26].
2.3 Other rates

The rate estimates for other processes like heating (excitation of higher trap eigenstates) and decoherence (decay of a superposition of magnetic sublevels into a statistical mixture) are discussed in the review paper by R. Folman and colleagues [31] and in the review by C. Henkel and the J. Schmiedmayer group [32]. The most robust choice for superposition states are magnetic sublevels that have the same magnetic moment. They are shifted in the same way by magnetic fluctuations so that their relative phase is preserved. Such states exists in alkali atoms, they have the same orientation of the electron spin and opposite nuclear spins. The difference in magnetic moment is only provided by the nuclear magneton which is much smaller than the Bohr magneton, by roughly the mass ratio between the nucleon and the electron.

Conclusion

Atoms are a sensitive probe of electromagnetic fields close to surfaces. Their energy level shifts depend on the reflection or scattering of the field from the surface, integrated over the entire frequency range. At short distances, the range around atomic transition frequencies gives the dominant contribution. This can lead, for a “hot” surface, to interesting non-equilibrium forces.

Transitions between different “internal” atomic states or the heating in a trap close to a surface gives directly access to the field’s cross spectral density at the transition frequency, provided perturbation theory holds. In magnetic traps that confine only a subset of Zeeman sublevels, the magnetic spectrum is the dominant driving agent for transitions and leads to trap loss, heating, and decoherence. The corresponding rates show different characteristic scalings with distance and substrate geometry, depending on the size of the skin depth inside the material.

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