THE ORIGIN OF VAN-DER-WAALS FORCES

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SECTION 1

Introduction to dispersion forces

This lecture series is dedicated to the general topic of dispersion forces: van-der-Waals forces, Casimir–Polder forces and Casimir forces. We will focus mainly on van-der-Waals forces and dive into the underlying theory of macroscopic quantum electrodynamics to generate a fundamental understanding and see which consequences we can find, for instance, by looking at large particle separations or by adding further objects such as a third molecule, a solid dielectric surface, or a solvent. But first, let us recap your knowledge about van-der-Waals forces.

1.1 Van-der-Waals forces and the four fundamental forces

Task 1.1 What do you know about van-der-Waals forces?

- Force between neutral particles (atoms, molecules, ...)
- Attractive force
- $U = -C_6/r^6$

Let us have a closer look at these statements:

The van-der-Waals force acts between neutral particles. We know the four fundamental forces; see table 1: gravity, electromagnetism, and weak and strong interactions. Where do we have to locate the van-der-Waals forces? The weak and strong interactions cannot cause it because the typical range is on the nanometre to micrometre scale $(10^{-9} \dots 10^{-6}\,\mathrm{m})$. Furthermore, it cannot be related to electromagnetism because the interacting objects are neutral. Hence there are no charges involved. Finally, is it gravity? – It cannot be gravity because van-der-Waals forces are much stronger than gravity forces. But what does it mean? Is there a fifth force, which is not known right now?[1] The short answer is "No!". The longer one is "Not observed until now. The experimental and theoretical error bars still overlap that one does not find a mismatch with the current precision." Concerning the location of van-der-Waals forces within the fundamental forces, it belongs to the electromagnetic forces. Still, it is hidden in the classical picture illustrated in table 1.

	Gravity	Electromagnetism	Weak interaction	Strong interaction
Acting on	mass	charges	quarks and leptons	quarks
Range	∞	∞	$< 10^{-17}\,\mathrm{m}$	$\approx 10^{-15}\,\mathrm{m}$
Rel. strength	1	10^{36}	10^{25}	10^{38}
Long-range	$1/r$	$1/r$	e^{-mr}/r	r

Table 1: Overview of the fundamental interactions: gravity, electromagnetism, weak and strong interactions concerning the corresponding property of the interaction objects (acting on), their range, their relative strength (rel. strength) compared to gravity, and their long-range behaviour.

The van-der-Waals force is attractive. Is this always the case? In the typical situation where two ground-state neutral point-like particles are brought together in a vacuum, the resulting force is always attractive. However, we can see the restrictions to the attraction of two particles. By (i) changing the environment from a vacuum to a liquid [1], (ii) considering anisotropic particles [2], or by (iii) considering excited particles [3], van-der-Waals forces can be turned repulsive.

The van-der-Waals potential has a $1/r^6$ dependency. The non-retarded limit (at short distances) of the van-der-Waals potential follows an r^{-6} power law. However, for longer separations, it turns to a r^{-7} power law, the so-called retarded regime [4]. In addition, at more minor separations close to binding distances, higher-order contributions start playing a role that turns the potential into a r^{-3} power law, known from the Casimir–Polder and Casimir potentials.

What determines the strength of the van-der-Waals forces? The van-der-Waals (C_6) coefficient denotes the strength of the force. One can assume that this force is not the same for all particles. This yields the question about the material properties determining the C_6 coefficient.

During the following lectures, we will examine these different questions about the van-der-Waals forces. We have now seen the limits of the van-der-Waals potential with the simple power law. In the following, we will derive this interaction from fundamental

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[1] There are considerations about the existence of a fifth force, see for instance: J. L. Feng *et al.* Phys. Rev. Lett. **117**, 071803 (2016).

principles and see how we can reproduce the known properties, how we can quantify the limits mentioned above, and what we can learn beyond.
Within these first lines of the text, we already received several keywords:

Definition 1.1.1

Van-der-Waals forces are forces between **neutral particles**, such as atoms and molecules. It is an **electromagnetic effect**. At short separations, it follows an r^{-6} power law (**non-retarded** regime). Its strength depends on the material properties.

1.2 Properties of atoms and molecules

Task 1.2 How do we distinguish between different particles?

Assume you get an unknown sample, either a gas, a liquid, or a solid. How do you find out its chemical components? Which devices can you apply?

- Techniques: Chromatography, mass spectroscopy
- Physical quantities: material-specific excitations, mass

Typical investigation methods to distinguish between chemical components are based on the emission or absorption spectra. The electromagnetic spectrum is unique for each material. A molecular system is described by an infinite set of wave functions $\{\psi_n\}$ and the associated energies[2] $\{E_n\}$ solving the stationary Schrödinger equation

$$\hat{H}\psi_n = E_n\psi_n\,, \tag{1}$$

with the molecular Hamiltonian

$$\hat{H} = \hat{T}_c + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{cc} + \hat{V}_{ec}\,, \tag{2}$$

which separates into the kinetic energy of the *c*ore $\hat{T}_c$ and of the *e*lectrons $\hat{T}_e$ and the interaction potential between the electrons $\hat{V}_{ee}$, between the cores $\hat{V}_{cc}$ and between the cores and the electrons $\hat{V}_{ec}$. For this lecture series, we do not care about the explicit solutions of Eq. (2). Several methods are available to solve the Schrödinger equation, such as density functional theory.

Definition 1.2.1

Properties of wave functions: The wave function is a complex probability distribution, which means that they are normalised

$$\int \mathrm{d}^3 r\, \psi_n^\star(r)\psi_n(r) = 1\,. \tag{3}$$

Furthermore, we assume the corresponding energy eigenvalues to be non-

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[2] Note that we consider atomic state leading to a discrete set of energy eigenvalues. For larger molecules, the energy eigenvalues turn from a discrete set to a continuous energy spectrum, leading to more complex equations of similar content.

degenerated, meaning that they are pairwise distinct

$$E_0 < E_1 < E_2 < \dots . \tag{4}$$

This property yields the orthogonality of the wave functions, which reads as

$$\int \mathrm{d}^3 r \, \psi_n^\star(r) \psi_m(r) = \delta_{nm} \,, \tag{5}$$

with the Kronecker delta

$$\delta_{nm} = \begin{cases} 1\,, & \text{if}\, n = m \\ 0\,, & \text{else} \end{cases} . \tag{6}$$

One commonly uses a shorter notation for the wave function, known as bra–ket notation or Dirac notation

$$\begin{aligned} \text{bra vector:} \quad & \psi_n(r) \mapsto |n\rangle \\ \text{ket vector:} \quad & \psi_m^\star(r) \mapsto \langle m| \end{aligned}$$

The bracket

$$\langle n|m\rangle = \int \mathrm{d}^3 r \, \psi_n^\star(r) \psi_m(r) = \delta_{nm} \tag{7}$$

denotes the dot product. One way to understand this notation is related to vector operations. The ket vector corresponds to a column vector

$$|n\rangle = \begin{pmatrix} n_1 \\ n_2 \\ \vdots \\ n_N \end{pmatrix} , \tag{8}$$

and the bra vector to a row vector

$$\langle m| = \begin{pmatrix} m_1^\star & m_2^\star & \dots & m_N^\star \end{pmatrix} , \tag{9}$$

illustrating the relation of the dot product according to matrix multiplications. In this picture, we can easily see that a scalar quantity, such as energies E_n, corresponds to measurement results; a vectorial quantity, $|n\rangle$, corresponds to states; and, when we look at the Schrödinger equation, $\hat{H}|n\rangle = E_n|n\rangle$, that a matrix corresponds to an operator. Furthermore, the measurement result and the matrix are related to each other: each measurable quantity A has its unique operator $\hat{A}$

$$A = \left\langle n|\hat{A}|n \right\rangle . \tag{10}$$

When we now come back to the Schrödinger equation for the free particle, it reads in Dirac notation

$$\hat{H}|n\rangle = E_n|n\rangle . \tag{11}$$

By multiplying this equation with the bra vector $\langle n|$ for the right and summing over all states, this equation transforms to

$$\sum_n \hat{H}\,|n\rangle\,\langle n| = \sum_n E_n\,|n\rangle\,\langle n|\,. \tag{12}$$

The Hamilton operator is independent of the state $|n\rangle$, and thus, the sum commutes with the Hamiltonian

$$\hat{H}\underbrace{\sum_n |n\rangle\,\langle n|}_{=\hat{1}} = \boxed{\hat{H} = \sum_n E_n\,|n\rangle\,\langle n|\,.} \tag{13}$$

As the sum over all projection operators $|n\rangle\,\langle n|$ yields the unitary operator; we have found the series expansion of the particle's Hamiltonian concerning the energy eigenvalues. Figure 1 illustrates the energy level scheme of an atom.

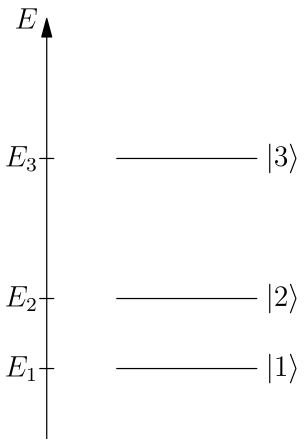

Figure 1: Energy levels of an atom.

We now have seen how the Hamiltonian of a free particle can be expanded in a series of eigenvalues and eigenvectors. At this point, its advantage is hard to recognise. It simplifies the following calculations because we do not need to worry about its explicit solutions. However, we initialised this part with the question about identifying different chemical components and mentioned that the electromagnetic response spectrum of each material is a unique fingerprint. On the microscopic level, the wave functions are special for each particle. To this end, a relationship between the microscopic wave functions and the macroscopic spectra has to exist, connecting this uniqueness over the different scales.

The complex dielectric function describes a macroscopic spectrum

$$\varepsilon(\omega) = \varepsilon'(\omega) + \mathrm{i}\varepsilon''(\omega)\,, \tag{14}$$

with its real and imaginary parts, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$. The existence of an imaginary part is a bit weird as we look at realistic materials. Its origin is realistic. When describing the optical properties of a solid surface, we consider its "colour", which is caused by the reflection of light and the absorption of light, typically leading to a warming of the object. When we want to describe both effects within one equation, it is useful to introduce a complex refractive index $n(\omega) = n'(\omega) + \mathrm{i}n''(\omega)$. A propagation wave, propagating in the direction $\boldsymbol{e}_k$, is described by

$$\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{E}_0 \mathrm{e}^{-\mathrm{i}\left(\omega t - \frac{\omega}{c} n(\omega)\boldsymbol{r}\cdot\boldsymbol{e}_k\right)}\,. \tag{15}$$

By inserting the complex refractive index, its imaginary part factorises out

$$\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{E}_0 \mathrm{e}^{-\mathrm{i}\left(\omega t - \frac{\omega}{c} n'(\omega)\boldsymbol{r}\cdot\boldsymbol{e}_k\right)} \mathrm{e}^{-\frac{\omega}{c} n''(\omega)\boldsymbol{r}\cdot\boldsymbol{e}_k}\,, \tag{16}$$

leading to the damping of the wave. Thus, the imaginary part of the refractive index is called the absorption coefficient. Due to the relation between refractive index and dielectric function

$$n(\omega) = \sqrt{\varepsilon(\omega)}\,, \tag{17}$$

the dielectric function is complex as well.

The dielectric function $\varepsilon(\omega)$ is traditionally considered as a macroscopic quantity, and thus it cannot be related to microscopic properties directly. In a broader sense, the dielectric function is an intensive property that does not scale with the extension of the object. The corresponding extensive quantity is the polarisability $\alpha(\omega)$. Both quantities are related to each other via the Clausius–Mossotti relation

$$\frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} = \sum_{i=1}^{\mathcal{N}} \frac{N_i \alpha_i(\omega)}{3\varepsilon_0}\,, \tag{18}$$

which is the extension to $\mathcal{N}$ components (Lorentz–Lorenz model), with the vacuum permittivity ε_0, the number density of the ith component N_i and its molecular polarisability $\alpha_i(\omega)$.[3]

The polarisability $\alpha(\omega)$ characterises the electromagnetic response of a particle by applying an external electric field $\boldsymbol{E}$ via inducing a dipole moment

$$\boldsymbol{d} = \boldsymbol{\alpha}\cdot\boldsymbol{E}\,. \tag{19}$$

It is usually a tensorial quantity. However, in the following, we restrict ourselves to the consideration of isotropic polarisabilities

$$\boldsymbol{\alpha} = \alpha\mathbb{I}\,, \tag{20}$$

with the three-dimensional unit-matrix, $\mathbb{I} = \operatorname{diag}(1,1,1)$. The frequency-dependence of the polarisability of a particle excited to the nth state is commonly described as a series of Lorentz oscillators

$$\alpha_n(\omega) = \frac{1}{\hbar}\sum_k \left[\frac{\boldsymbol{d}_{nk}\boldsymbol{d}_{kn}}{\omega_{kn}-\omega-\frac{\mathrm{i}}{2}(\Gamma_n+\Gamma_k)} + \frac{\boldsymbol{d}_{kn}\boldsymbol{d}_{nk}}{\omega_{kn}+\omega+\frac{\mathrm{i}}{2}(\Gamma_n+\Gamma_k)}\right]\,, \tag{21}$$

with the reduced Planck constant $\hbar$, the transition dipole moments

$$\boldsymbol{d}_{nm} = \langle m|\,\hat{\boldsymbol{d}}\,|n\rangle = e\,\langle m|\,\hat{\boldsymbol{r}}\,|n\rangle\,, \tag{22}$$

the resonance energies (respectively frequencies)

$$E_{mn} = \hbar\omega_{mn} = \hbar\,[E_n - E_m] = \hbar\left[\langle n|\,\hat{H}\,|n\rangle - \langle m|\,\hat{H}\,|m\rangle\right]\,, \tag{23}$$

and the decay rates

$$\Gamma_n = \sum_{m<n}\Gamma_{nm} = \sum_{m<n}\frac{\omega_{nm}^3\,|\boldsymbol{d}_{nm}|^2}{3\hbar\pi\varepsilon_0 c^3}\,, \tag{24}$$

which known as the Einstein coefficient or Fermi's golden rule.

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[3] Note that the considered volume is spherical, which can be seen in the Mie reflection coefficient on the left-hand side of the equation, see for instance J.D. Jackson *Classical Electrodynamics* – Chapter 4: Multipoles, Electrostatics of Macroscopic Media, Dielectrics.

Task 1.3 Typical strength of a transition dipole moment?

The dipole moment d is charge q times charge separation r, $d = qr$. A typical charge in an atom is an electron $q = e$, and the typical separations are related to the Bohr radius $r = a_\mathrm{B}$. Hence, $d = 1.6 \cdot 10^{-19}\,\mathrm{C} \times 5.3 \cdot 10^{-11}\,\mathrm{m} \approx 8.48 \cdot 10^{-30}\,\mathrm{Cm}$.
Polarisability: optical frequency $\nu = \mathcal{O}\left(10^{14}\,\mathrm{Hz}\right)$
$\rightarrow \alpha \approx \frac{1}{6.626 \cdot 10^{-34}\mathrm{Js}} \times \left(8.48 \cdot 10^{-30}\,\mathrm{Cm}\right)^2 \times \frac{1}{10^{14}\mathrm{Hz}} = 1.1 \cdot 10^{-39}\,\mathrm{C^2m^2/J} = 1.1 \cdot 10^{-39}\,\mathrm{Cm^2/V}$

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SECTION

Quantisation of the electromagnetic fields

In the last lecture, we saw that the van-der-Waals forces occur between polarisable particles and are mediated via the electromagnetic field. This means that classically, we would need a permanent electromagnetic field inducing dipole moments in the molecules that can interact. However, we also know that the van-der-Waals forces also arise in the absence of electromagnetic fields. Thus, we need another mechanism to induce the dipole moments.

Task 2.1 Dimension analysis of the Casimir force

The Casimir force is an attractive force between two parallel perfectly conducting plates. We already know that the force is a quantum effect, thus the force density, $[F/A] = \mathrm{N/m^2}$, should depend on the Planck constant, $[\hbar] = \mathrm{Js}$. Furthermore, it is a vacuum-electromagnetic effect, meaning that it should include the speed of light, $[c] = \mathrm{m/s}$. Which power law scales the Casimir force density with the distance $[d] = \mathrm{m}$?

$$\begin{aligned} [\hbar \cdot c] &= \mathrm{Jm} = \mathrm{Nm^2} \\ \left[\frac{\hbar}{c}\right] &= \mathrm{Js^2/m} = \mathrm{Nms^2} \end{aligned}$$

Obviously, the product between $\hbar$ and c needs to be chosen to get rid of the time. Furthermore, the force density has to be proportional to this product

$$\frac{F}{A} \propto \hbar c d^n \,. \tag{25}$$

Finally, the units of this equation are

$$\mathrm{N/m^2} = \mathrm{Nm^{2+n}}\,,$$

hence, the force density scales with a d^{-4} power law

$$\frac{F}{A} = \frac{\pi^2}{240}\hbar c \frac{1}{d^4}\,. \tag{26}$$

2.1 Maxwell's equations

The microscopic Maxwell's equations are:

Gauss's law describes the relationship between a static electric field and electric charges: a static electric field points away from positive charges and towards negative charges, and the net outflow of the electric field through a closed surface is proportional to the enclosed charge, including bound charge due to polarisation of material. The coefficient of the proportion is the permittivity of free space

$$\nabla \cdot \boldsymbol{E}(\boldsymbol{r}) = \frac{\varrho(\boldsymbol{r})}{\varepsilon_0}\,. \tag{27}$$

Gauss's law for magnetism states that electric charges have no magnetic analogues, called magnetic monopoles, i.e. no single pole exists. Instead, the magnetic field of a material is attributed to a dipole, and the net outflow of the magnetic field through a closed surface is zero. Magnetic dipoles may be represented as loops of current or inseparable pairs of equal and opposite "magnetic charges". The total magnetic flux through a Gaussian surface is zero, and the magnetic field is a solenoidal vector field

$$\nabla \cdot \boldsymbol{B}(\boldsymbol{r}) = 0\,. \tag{28}$$

Faraday's law describes how a time-varying magnetic field corresponds to the curl of an electric field

$$\nabla \times \boldsymbol{E}(\boldsymbol{r}) = -\dot{\boldsymbol{B}}(\boldsymbol{r})\,. \tag{29}$$

Ampère's law with Maxwell's addition: The original law of Ampère states that magnetic fields relate to electric current. Maxwell's addition states that they also relate to changing electric fields, which Maxwell called displacement current

$$\nabla \times \boldsymbol{B}(\boldsymbol{r}) = \mu_0 \varepsilon_0 \dot{\boldsymbol{E}}(\boldsymbol{r}) + \mu_0 \boldsymbol{J}(\boldsymbol{r})\,. \tag{30}$$

The set of these four equations (27)-(30) describes the propagation of electromagnetic fields within a given system.

2.1.1 Electrodynamics in free space

In the absence of charges $\varrho(\boldsymbol{r}) = 0$ and currents $\boldsymbol{J}(\boldsymbol{r}) = \boldsymbol{0}$, the Maxwell equations simplifies to

$$\nabla \cdot \boldsymbol{E}(\boldsymbol{r}) = 0\,, \tag{31}$$

$$\nabla \cdot \boldsymbol{B}(\boldsymbol{r}) = 0\,, \tag{32}$$

$$\nabla \times \boldsymbol{E}(\boldsymbol{r}) + \dot{\boldsymbol{B}}(\boldsymbol{r}) = \boldsymbol{0}\,, \tag{33}$$

$$\nabla \times \boldsymbol{B}(\boldsymbol{r}) - \frac{1}{c^2}\dot{\boldsymbol{B}}(\boldsymbol{r}) = \boldsymbol{0}\,, \tag{34}$$

where we used $\varepsilon_0 \mu_0 = c^{-2}$. To simplify this system of equations, we introduce the scalar potential $\varphi(\boldsymbol{r})$ and the vector potential $\boldsymbol{A}(\boldsymbol{r})$ according to

$$\boldsymbol{E}(\boldsymbol{r}) = -\nabla\varphi(\boldsymbol{r}) - \dot{\boldsymbol{A}}(\boldsymbol{r}) \tag{35}$$

$$\boldsymbol{B}(\boldsymbol{r}) = \nabla \times \boldsymbol{A}(\boldsymbol{r})\,. \tag{36}$$

Thus, eqs. (32) and (33) are automatically fulfilled, and the remaining equations yield to

$$-\Delta\varphi(\boldsymbol{r}) - \nabla \cdot \dot{\boldsymbol{A}}(\boldsymbol{r}) = 0\,, \tag{37}$$

$$\frac{1}{c^2}\nabla\dot{\varphi}(\boldsymbol{r}) + \frac{1}{c^2}\ddot{\boldsymbol{A}}(\boldsymbol{r}) - \Delta\boldsymbol{A}(\boldsymbol{r}) + \nabla\left[\nabla \cdot \boldsymbol{A}(\boldsymbol{r})\right] = \boldsymbol{0}\,. \tag{38}$$

Note that potentials are never unique. For instance, potential forces $\boldsymbol{F}(\boldsymbol{r}) = -\nabla U(\boldsymbol{r})$. When we add constant energy E to the potential $U(\boldsymbol{r}) \mapsto U(\boldsymbol{r}) + E$, the force does not change because $\nabla E = \boldsymbol{0}$. In the case of the scalar and vector potentials, this "constant" is expressed by an arbitrary scalar field $\Lambda(\boldsymbol{r})$ transforming the scalar and vector potentials via

$$\varphi(\boldsymbol{r}) \mapsto \varphi(\boldsymbol{r}) - \dot{\Lambda}(\boldsymbol{r})\,, \tag{39}$$

$$\boldsymbol{A}(\boldsymbol{r}) \mapsto \boldsymbol{A}(\boldsymbol{r}) + \nabla\Lambda(\boldsymbol{r})\,. \tag{40}$$

This is a gauge transformation and introduces an additional degree of freedom to simplify the equations. In non-relativistic electrodynamics, it is commonly employed the Coulomb gauge

$$\nabla \cdot \boldsymbol{A}(\boldsymbol{r}) = 0\,. \tag{41}$$

This gauge is often referred to as the transverse gauge, which is motivated by the fact that electromagnetic waves in free space only have transversal components meaning that the wave oscillates perpendicular to the direction of the propagation $\boldsymbol{k}$. The relation between this fact and the gauge (41) can be seen by its transformation into Fourier space

$$\boldsymbol{k} \cdot \boldsymbol{A}(\boldsymbol{k}) = 0\,. \tag{42}$$

Definition 2.1.1

Vector algebra

A plane is given by the equation

$$ax + bc + cz + d = 0\,, \tag{43}$$

with the off-set $d = -ax_0 - by_0 - cz_0$. Furthermore, a plane is characterised by its **normal** vector

$$\boldsymbol{n} = \begin{pmatrix} a \\ b \\ c \end{pmatrix} . \tag{44}$$

Thus, a plane can also be given via

$$\left[\begin{pmatrix} x \\ y \\ z \end{pmatrix} - \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix}\right] \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix} = 0 = [\boldsymbol{r} - \boldsymbol{r}_0] \cdot \boldsymbol{n} , \tag{45}$$

meaning that all points $\boldsymbol{r}$ belong to the plane whose relative vectors (relative to a point in the plane $\boldsymbol{r}_0$) are orthogonal to the normal vector.

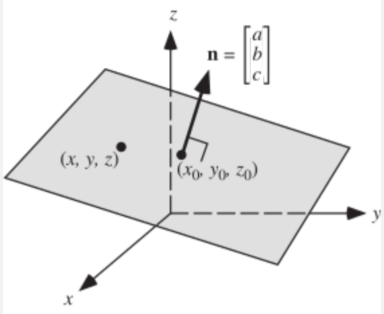

Figure 2: Normal vector of a plane. Figure taken from https://mathworld.wolfram.com/Plane.html

Hence, Equation (42) means that the vector potential is orthogonal to the wave vector, which we denote as transverse.

By applying the Coulomb gauge (41) to the field equations (37) and (38), they reduce to an uncoupled Laplace equation

$$\Delta\varphi(\boldsymbol{r}) = 0 , \tag{46}$$

and a Helmholtz equation

$$\frac{1}{c^2}\ddot{\boldsymbol{A}}(\boldsymbol{r}) - \Delta\boldsymbol{A}(\boldsymbol{r}) = \boldsymbol{0} . \tag{47}$$

The solutions of the Helmholtz equation are plane waves

$$\boldsymbol{A}(\boldsymbol{r},t) = \sum_{\sigma=1}^{2} \int \frac{\mathrm{d}^3 k}{(2\pi)^{3/2}} \boldsymbol{e}_\sigma(\boldsymbol{k})\,\omega \left[u_{\boldsymbol{k}\sigma} \mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} + u^*_{\boldsymbol{k}\sigma} \mathrm{e}^{-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} \right] , \tag{48}$$

with the two polarisation vectors $\boldsymbol{e}_\sigma$ ($\sigma = 1,2$) spanning the plane orthogonal to the wave vector $\boldsymbol{k}$ and the amplitude of the partial waves $u_{\boldsymbol{k}\sigma}$.[4]

The energy of the field is given by the Hamilton function (or Hamiltonian)

$$H = \frac{1}{2}\int \mathrm{d}^3 r \left[\varepsilon_0 \boldsymbol{E}^2(\boldsymbol{r}) + \frac{1}{\mu_0}\boldsymbol{B}^2(\boldsymbol{r}) \right] . \tag{49}$$

Plugging in the Coulomb gauge (41) and using the orthogonality of the polarisation vectors $\boldsymbol{e}_\sigma \cdot \boldsymbol{e}_{\sigma'} = \delta_{\sigma\sigma'}$ and the relation $(\boldsymbol{k} \times \boldsymbol{e}_\sigma) \cdot (\boldsymbol{k} \times \boldsymbol{e}_{\sigma'}) = k^2 (\boldsymbol{e}_\sigma \cdot \boldsymbol{e}_{\sigma'}) = k^2 \delta_{\sigma\sigma'}$, leaves us with

$$H = 2\varepsilon_0 \sum_{\sigma=1}^{2} \int \mathrm{d}^3 k \omega^2 |u_{\boldsymbol{k}\sigma}|^2 . \tag{50}$$

These complex-valued functions $u_{\boldsymbol{k}\sigma}$ can be split into their real and imaginary parts

$$q_{\boldsymbol{k}\sigma} = \sqrt{\varepsilon_0}\left(u_{\boldsymbol{k}\sigma} + u^*_{\boldsymbol{k}\sigma}\right) , \quad p_{\boldsymbol{k}\sigma} = -\mathrm{i}\omega\sqrt{\varepsilon_0}\left(u_{\boldsymbol{k}\sigma} - u^*_{\boldsymbol{k}\sigma}\right) , \tag{51}$$

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[4] Note: real solutions of a wave equation consist of sin and cos function. Complex numbers help to simplify two equations into one $A = u\mathrm{e}^{\mathrm{i}\varphi} + u^*\mathrm{e}^{-\mathrm{i}\varphi} = u\mathrm{e}^{\mathrm{i}\varphi} + \left(u\mathrm{e}^{\mathrm{i}\varphi}\right)^* = 2\mathrm{Re}\left(u\mathrm{e}^{\mathrm{i}\varphi}\right)$. Thus, A is purely real, $A \in \mathbb{R}$.

which yields the classical Hamiltonian in the form

$$H = \frac{1}{2} \sum_{\sigma=1}^{2} \int \mathrm{d}^3 k \left(p_{\boldsymbol{k}\sigma}^2 + \omega^2 q_{\boldsymbol{k}\sigma}^2 \right) . \tag{52}$$

Thus, we have converted the Hamiltonian for the free electromagnetic field (49) into an infinite sum of uncoupled harmonic oscillators with frequencies $\omega = kc$. The functions $q_{\boldsymbol{k}\sigma}$ and $p_{\boldsymbol{k}\sigma}$ are thus analogous to the position and momentum of a classical particle of mass m attached to a spring with spring constant $D = m\omega^2$.

Definition 2.1.2

The classical harmonic oscillator describes the motion of a particle in a quadratic potential $V(x) = \frac{1}{2}Dx^2$ with spring constant D. To derive the equation of motion, we start with the Hamiltonian of the system. The Hamiltonian describes the total energy of the system, and in the case of a particle of mass m, it consists of two parts - the kinetic energy T and the potential energy V,

$$H = T + V . \tag{53}$$

The kinetic energy is given by the momentum of the particle p

$$T = \frac{p^2}{2m} . \tag{54}$$

Thus, the Hamiltonian reads

$$H = \frac{p^2}{2m} + \frac{1}{2} D x^2 . \tag{55}$$

The corresponding equations of motion are according to Newton's laws:

The momentum change is given by force acting on the particle

$$\dot{p} = -\frac{\mathrm{d}V}{\mathrm{d}x} , \tag{56}$$

and,

The position change is given by the momentum acting on the particle

$$\dot{x} = \frac{p}{m} . \tag{57}$$

Combining both equations, we derived the equation of motion for the harmonic oscillator

$$\ddot{x} = -\frac{1}{m}\frac{\mathrm{d}V}{\mathrm{d}x} = -\frac{1}{m} D x . \tag{58}$$

By looking closer to the unit of the spring constant $[D] = \mathrm{N/m} = \mathrm{kg/s^2}$, we can see that the prefactor D/m has a unit of a frequency square $[D/m] = 1/\mathrm{s}^2 = \mathrm{Hz}^2$. Thus, we can define the frequency of the harmonic oscillator via $\omega = \sqrt{D/m}$. To this end, the equation of motion reads as

$$\ddot{x} = -\omega^2 x . \tag{59}$$

When we neglect the prefactor, we observe that this differential equation means that we have to differentiate a function twice and obtain the same function with a minus sign in front. Two functions fulfil this relation — Sine sin and Cosine cos,

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\sin x = -\sin x\,, \quad \frac{\mathrm{d}^2}{\mathrm{d}x^2}\cos x = -\cos x\,. \tag{60}$$

By using the chain rule to include the frequency ω, we see that the solutions are harmonic oscillation

$$x(t) = C_1 \sin\omega t + C_2 \cos\omega t\,. \tag{61}$$

Take home message

A harmonic oscillator always has a Hamiltonian of the form

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2\,, \tag{62}$$

quadratic in p and quadratic in x.

Task 2.2 Canonical transformation of the harmonic oscillator

Consider the transformation of the variables

$$\begin{aligned} a &= \frac{p}{\sqrt{2m\omega}} - \mathrm{i}\frac{m\omega x}{\sqrt{2m\omega}}\,, \\ a^* &= \frac{p}{\sqrt{2m\omega}} + \mathrm{i}\frac{m\omega x}{\sqrt{2m\omega}}\,, \end{aligned}$$

and transform the Hamiltonian (62) into the complex plain.
Solving the system of equations to get expressions for p and x

$$\begin{aligned} p &= \sqrt{\frac{m\omega}{2}}\left(a + a^*\right)\,, \\ x &= \mathrm{i}\frac{1}{\sqrt{2m\omega}}\left(a - a^*\right)\,. \end{aligned}$$

And inserting the result into the Hamiltonian yields

$$H = \omega a a^* = \omega\,|a|^2\,. \tag{63}$$

Take home message

A harmonic oscillator can always be expressed via a complex Hamiltonian of the form

$$H = \omega\,|a|^2\,, \tag{64}$$

with complex amplitude a, whose real part is proportional to the momentum and imaginary part to the position.

2.1.2 General solutions via dyadic Green function

In the previous section, we derived the mode structure for the vacuum (in the absence of charges and currents). To include the presence of absorbing materials, one needs to solve the Maxwell equations (27)–(30) for a given system. The Maxwell equations in this form are charged-based due to the explicit consideration of charge density $\varrho(\boldsymbol{r})$ and charge density current $\boldsymbol{j}(\boldsymbol{r})$. To introduce dielectric objects, one separates the charges into free and bounded charge density

$$\varrho(\boldsymbol{r}) = \varrho_{\text{free}}(\boldsymbol{r}) + \varrho_{\text{bound}}(\boldsymbol{r}), \tag{65}$$

analogously for the currents. The bounded charges are considered as a source for the polarisation

$$\nabla\dot{\boldsymbol{P}}(\boldsymbol{r}) = \varrho_{\text{bound}}(\boldsymbol{r}). \tag{66}$$

The continuity equation and the corresponding current yield the magnetisation

$$\boldsymbol{j}_{\text{bound}}(\boldsymbol{r}) = \nabla\times\boldsymbol{M}(\boldsymbol{r}) + \dot{\boldsymbol{P}}(\boldsymbol{r}). \tag{67}$$

Thus, we can absorb the consideration of the bounded charges by adding the polarisation $\boldsymbol{P}$ and magnetisation $\boldsymbol{M}$ to the electric and magnetic fields, leading the displacement field

$$\boldsymbol{D}(\boldsymbol{r}) = \varepsilon_0\boldsymbol{E}(\boldsymbol{r}) + \boldsymbol{P}(\boldsymbol{r}), \tag{68}$$

and the magnetisation field

$$\boldsymbol{H}(\boldsymbol{r}) = \frac{1}{\mu_0}\boldsymbol{B}(\boldsymbol{r}) - \boldsymbol{M}(\boldsymbol{r}). \tag{69}$$

Thus, we can write the macroscopic Maxwell equations

$$\nabla\cdot\boldsymbol{D}(\boldsymbol{r}) = \varrho_{\text{free}}(\boldsymbol{r}), \tag{70}$$

$$\nabla\cdot\boldsymbol{B}(\boldsymbol{r}) = 0, \tag{71}$$

$$\nabla\times\boldsymbol{E}(\boldsymbol{r}) = -\dot{\boldsymbol{B}}(\boldsymbol{r}), \tag{72}$$

$$\nabla\times\boldsymbol{H}(\boldsymbol{r}) = \boldsymbol{j}_{\text{free}}(\boldsymbol{r}) + \dot{\boldsymbol{D}}(\boldsymbol{r}). \tag{73}$$

Assuming that the medium responds linearly and locally to externally applied fields, we can write their responses in the form

$$\boldsymbol{P}(\boldsymbol{r},t) = \varepsilon_0\int_0^\infty \mathrm{d}\tau\,\chi_{\mathrm{e}}(\boldsymbol{r},\tau)\boldsymbol{E}(\boldsymbol{r},t-\tau), \tag{74}$$

$$\boldsymbol{M}(\boldsymbol{r},t) = \frac{1}{\mu_0}\int_0^\infty \mathrm{d}\tau\,\chi_{\mathrm{m}}(\boldsymbol{r},\tau)\boldsymbol{B}(\boldsymbol{r},t-\tau), \tag{75}$$

with the electric and magnetic media response functions χ_{e} and χ_{m}, respectively.

We need to have conditions for unique solutions to solve this system of differential equations for a given geometry. These conditions are the so-called Maxwell boundary conditions which mean the continuation of the fields at interfaces and read

$$\boldsymbol{n}_{12} \times (\boldsymbol{E}_2 - \boldsymbol{E}_1) = \boldsymbol{0}\,, \tag{76}$$

$$\boldsymbol{n}_{12} \cdot (\boldsymbol{D}_2 - \boldsymbol{D}_1) = \sigma_{12}\,, \tag{77}$$

$$\boldsymbol{n}_{12} \cdot (\boldsymbol{B}_2 - \boldsymbol{B}_1) = 0\,, \tag{78}$$

$$\boldsymbol{n}_{12} \times (\boldsymbol{H}_2 - \boldsymbol{H}_1) = \boldsymbol{j}_{12}\,, \tag{79}$$

with the normal vector of the interface $\boldsymbol{n}_{12}$, the surface charge density σ_{12} and the surface current density $\boldsymbol{j}_{12}$. Finally, when we want to consider a specific system, we need to solve this system of equations together with the boundary conditions. To stay as general as possible, we first consider the temporal Fourier transform of the Maxwell equations

$$\nabla \cdot \boldsymbol{D}(\boldsymbol{r}) = \varrho_{\text{free}}(\boldsymbol{r})\,, \tag{80}$$

$$\nabla \cdot \boldsymbol{B}(\boldsymbol{r}) = 0\,, \tag{81}$$

$$\nabla \times \boldsymbol{E}(\boldsymbol{r}) = \mathrm{i}\omega \boldsymbol{B}(\boldsymbol{r})\,, \tag{82}$$

$$\nabla \times \boldsymbol{H}(\boldsymbol{r}) = \boldsymbol{j}_{\text{free}}(\boldsymbol{r}) - \mathrm{i}\omega \boldsymbol{D}(\boldsymbol{r})\,. \tag{83}$$

Now, we can plug in the displacement field (68) and the magnetisation field (69) into (83) leading to

$$\nabla \times \left[\frac{1-\chi_{\mathrm{M}}(\boldsymbol{r})}{\mu_0}\boldsymbol{B}(\boldsymbol{r})\right] = \boldsymbol{j}_{\text{free}}(\boldsymbol{r}) - \mathrm{i}\omega\varepsilon_0\left(1+\chi_{\mathrm{E}}(\boldsymbol{r})\right)\boldsymbol{E}(\boldsymbol{r})\,. \tag{84}$$

By introducing

$$\varepsilon(\boldsymbol{r},\omega) = 1 + \chi_{\mathrm{E}}(\boldsymbol{r},\omega)\,, \quad \mu(\boldsymbol{r},\omega) = \frac{1}{1-\chi_{\mathrm{M}}(\boldsymbol{r},\omega)}\,, \tag{85}$$

and substituting the magnetic field $\boldsymbol{B}$ via Eq. (82), we obtain the vector Helmholtz equation

$$\nabla\times\frac{1}{\mu(\boldsymbol{r},\omega)}\nabla\times\boldsymbol{E}(\boldsymbol{r},\omega) - \frac{\omega^2\varepsilon(\boldsymbol{r},\omega)}{c^2}\boldsymbol{E}(\boldsymbol{r},\omega) = \mathrm{i}\omega\boldsymbol{j}_{\text{free}}(\omega)\,, \tag{86}$$

whose solution can be written as

$$\boldsymbol{E}(\boldsymbol{r},\omega) = \mathrm{i}\omega\int \mathrm{d}^3r'\,\mathbf{G}(\boldsymbol{r},\boldsymbol{r}',\omega)\cdot\boldsymbol{j}_{\text{free}}(\boldsymbol{r}')\,, \tag{87}$$

with the dyadic (tensorial) Green function obeying

$$\left[\nabla\times\frac{1}{\mu(\boldsymbol{r},\omega)}\nabla\times-\frac{\omega^2\varepsilon(\boldsymbol{r},\omega)}{c^2}\right]\mathbf{G}(\boldsymbol{r},\boldsymbol{r}',\omega) = \boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')\,. \tag{88}$$

The Green function techniques allow us to continue with theory without explicitly considering the fields of the specific system. Of course, when we want to apply this theory to any system, we need to take care of its solution. But for the moment, we found a way to express the complex solution of Maxwell's equations within one quantity.

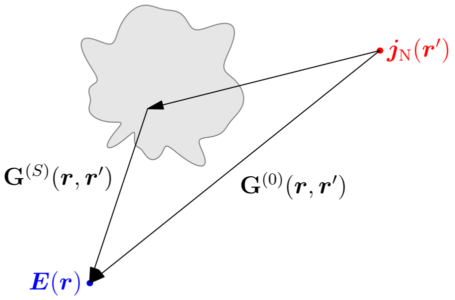

Figure 3: Separation of the Green function $\mathbf{G}$ into the free (bulk) propagation $\mathbf{G}^{(0)}$ and its scattering part $\mathbf{G}^{(S)}$.

The Green function is known as the field propagator. It has to be read from right to left, meaning that the source point is $\boldsymbol{r}'$ and the final point is $\boldsymbol{r}$. It can be separated into the free propagation $\mathbf{G}^{(0)}$ and its scattering part $\mathbf{G}^{(S)}$

$$\mathbf{G}(\boldsymbol{r},\boldsymbol{r}',\omega) = \mathbf{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) + \mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}',\omega)\,. \tag{89}$$

Figure 3 illustrates this separation.

2.1.3 Free-space Green function

One important solution of the vector Helmholtz equation is the free-space or bulk Green function, which describes the propagation in a spatially homogeneous medium $\varepsilon(\boldsymbol{r},\omega) = \varepsilon(\omega)$ and $\mu(\boldsymbol{r},\omega) = \mu(\omega)$. Thus, the Helmholtz equation simplifies to

$$\left[\nabla\times\nabla\times - k_0^2\right]\mathbf{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \mu(\omega)\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')\,, \tag{90}$$

with the wavevector

$$k_0 = \frac{\omega}{c}\sqrt{\varepsilon(\omega)\mu(\omega)}\,. \tag{91}$$

It can be seen that the Helmholtz equation only depends on relative coordinates $\boldsymbol{\varrho} = \boldsymbol{r}-\boldsymbol{r}'$ leading to a spatially local Green function $\mathbf{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \mathbf{G}^{(0)}(\boldsymbol{r}-\boldsymbol{r}',\omega)$. Defining the Fourier transform of the Green function

$$\mathbf{G}^{(0)}(\boldsymbol{k},\omega) = \int \frac{\mathrm{d}^3\varrho}{(2\pi)^{3/2}}\mathbf{G}^{(0)}(\boldsymbol{\varrho},\omega)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\varrho}}\,, \tag{92}$$

the Fourier transformed Helmholtz equation reads

$$-\boldsymbol{k}\times\boldsymbol{k}\times\mathbf{G}^{(0)}(\boldsymbol{k},\omega) - k_0^2\mathbf{G}^{(0)}(\boldsymbol{k},\omega) = \mu(\omega)\mathbf{1}\,, \tag{93}$$

with the three-dimensional unit matrix $\mathbf{1} = \mathrm{diag}(1,1,1)$.

Definition 2.1.3

Projection operator:

The projection of a vector $\boldsymbol{v}$ onto another vector $\boldsymbol{w}$ is the component of $\boldsymbol{v}$ into the direction of $\boldsymbol{w}$. Thus, we want to create a vector $\boldsymbol{v}_w$ pointing in the same direction as $\boldsymbol{w}$ having the length of the projection of $\boldsymbol{v}$ onto $\boldsymbol{w}$. The length can be determined by the dot product

$$l = \frac{\boldsymbol{w}\cdot\boldsymbol{v}}{|\boldsymbol{w}|}\,.$$

The direction is given by the unit vector corresponding to $\boldsymbol{w}$

$$\boldsymbol{e}_w = \frac{\boldsymbol{w}}{|\boldsymbol{w}|}\,.$$

Combining both, we can obtain the projection

$$\boldsymbol{v}_w = l\boldsymbol{e}_w = \frac{\boldsymbol{w}\cdot\boldsymbol{v}}{|\boldsymbol{w}|}\frac{\boldsymbol{w}}{|\boldsymbol{w}|} = w_i v_i\frac{w_j}{|\boldsymbol{w}|^2} = \frac{w_j w_i}{|\boldsymbol{w}|^2}v_i\,,$$

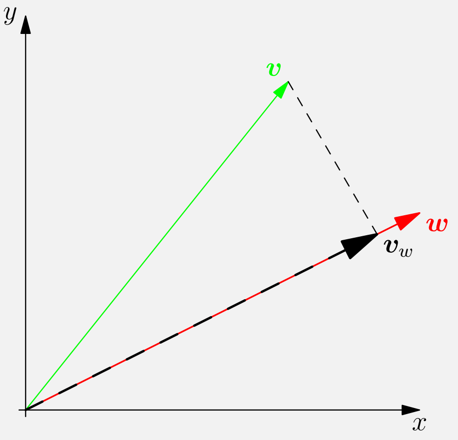

Figure 4: Projection of the vector $\boldsymbol{v}$ (green) on the vector $\boldsymbol{w}$ (red) yields the vector $\boldsymbol{v}_w$.

where we used the commutation of scalar quantities. The first term on the right-hand side has the structure of a matrix with the components

$$P_{ji} = \frac{w_j w_i}{|\boldsymbol{w}|^2}\,.$$

Thus, we can write the projection of the vector $\boldsymbol{v}$ as a matrix product

$$\boldsymbol{v}_w = \mathbf{P}_w\cdot\boldsymbol{v}\,, \tag{94}$$

with the projection operator

$$\mathbf{P}_w = \frac{\boldsymbol{w}\boldsymbol{w}}{|\boldsymbol{w}|^2}\,, \tag{95}$$

onto the vector $\boldsymbol{w}$. Such projection operators appear very often; for instance, the atom flip operator in the molecular Hamiltonian (13) projects any state onto the eigenbasis $|n\rangle$ (the denominator is one due to the normalisation of the state vectors).

By introducing the projection operator onto the wave vector $\boldsymbol{k}$

$$\mathbf{P}_k = \frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\,,$$

we can write the double cross product as

$$-\boldsymbol{k}\times\boldsymbol{k}\times = k^2\left(\mathbf{1}-\frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\right), \tag{96}$$

separating the field into its transverse components. Thus, we can write the bulk Green function as

$$\mathbf{G}^{(0)}(\boldsymbol{\varrho},\omega) = \mu(\omega)\int\frac{\mathrm{d}k^3\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\varrho}}}{(2\pi)^{3/2}}\left[\frac{1}{k^2-k_0^2}\left(\mathbf{1}-\frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\right)-\frac{1}{k_0^2}\frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\right]. \tag{97}$$

This integral can be carried out and yields

$$\mathbf{G}^{(0)}(\boldsymbol{\varrho},\omega) = -\frac{\mu(\omega)}{3k_0^2}\boldsymbol{\delta}(\boldsymbol{\varrho})-\frac{\mu(\omega)}{4\pi k_0^2\varrho^3}\left[f(k\varrho)\mathbf{1}-g(k\varrho)\frac{\boldsymbol{\varrho}\boldsymbol{\varrho}}{\varrho^2}\right]\mathrm{e}^{\mathrm{i}k_0\varrho}\,, \tag{98}$$

with $f(x) = 1-\mathrm{i}x-x^2$ and $g(x) = 3-\mathrm{i}x-x^2$.

2.2 Quantisation of the electromagnetic field

In the previous chapter, we discussed the classical Maxwell equation describing classical Electrodynamics and introduced the Green function as a general solution. Furthermore, we have already considered parts of the Hamiltonian mechanics for the electromagnetic field, which will be extended in this section to quantise the electromagnetic fields. Before we derive the quantised fields, we will take a special view on the linear response of a medium (74).

2.2.1 Fluctuation–Dissipation theorem

The response of a system R with respect to an external force F can be written in general as a convolution with its corresponding response function χ

$$R(t) = \int_{-\infty}^{t}\chi(t-t')F(t')\mathrm{d}t'\,. \tag{99}$$

The response function χ characterises the system. In the framework of differential equations, it describes the particular solution.

Definition 2.2.1

Linear response function of the harmonic oscillator:
The differential equation of the damped harmonic oscillator reads

$$\ddot{x} + 2\delta\dot{x} + \omega_0^2 x = f(t)\,, \tag{100}$$

with the damping constant δ, the angular frequency ω_0 and the driving force $f(t)$. Its solution can be written as the superposition of the solution homogeneous equation

$$\ddot{x} + 2\delta\dot{x} + \omega_0^2 x = 0\,, \tag{101}$$

and a particular solution of the inhomogeneous equation. The homogeneous solution can be found by applying the ansatz $x(t) = \mathrm{e}^{\lambda t}$ leading to the characteristic polynomial

$$\lambda^2 + 2\delta\lambda + \omega_0^2 = 0\,, \tag{102}$$

with the solution

$$\lambda_{1,2} = -\delta \pm \sqrt{\delta^2 - \omega_0^2}\,. \tag{103}$$

Thus, the homogeneous solution reads

$$x_{\text{hom}}(t) = C_1\mathrm{e}^{\lambda_1 t} + C_2\mathrm{e}^{\lambda_2 t}\,, \tag{104}$$

showing an exponential decay when the damping is stronger than the angular frequency $\delta \geq \omega_0$. The coefficients $C_{1,2}$ have to be fixed by the initial conditions. For the driven oscillator, one needs to add a particular solution, satisfying the entire differential equation. For a given driving force $f(t)$, one usually guesses a particular solution x_{part}. If one does not find a good guess, one applies Green function techniques

$$x_{\text{part}}(t) = \int_0^t \mathrm{d}t'\, g(t-t')f(t')\,, \tag{105}$$

where the Green function satisfies the differential equation

$$\ddot{g}(t) + 2\delta\dot{g}(t) + \omega_0^2 g(t) = \delta(t-t')\,. \tag{106}$$

Fourier transforming this equation, similar to the calculation of the bulk Green function in Sec. 2.1.3, we transform the differential equation into an algebraic equation

$$-\omega^2 g(\omega) + 2\delta\mathrm{i}\omega g(\omega) + \omega_0^2 g(\omega) = \frac{1}{\sqrt{2\pi}}\,. \tag{107}$$

Finally, we find the response function in Fourier space

$$g(\omega) = \frac{1}{\sqrt{2\pi}}\frac{1}{\omega_0^2 - \omega^2 + 2\mathrm{i}\delta\omega}\,. \tag{108}$$

Here, we can see that the response function has an imaginary part related to the oscillator's damping. Damping is a dissipative process that is connected to energy loss.

In the previous definition box, we have seen that a dissipative system always has a complex-valued response function, $\operatorname{Im}(\chi) \neq 0$.
Every quantity A can be separated into a mean-value $\langle A \rangle$ and a fluctuation A'

$$A = \langle A \rangle + A', \tag{109}$$

where different methods exist to estimate the mean value, see table 2.

Time-average	$\langle A(t) \rangle = \frac{1}{\tau} \int\limits_{t-\tau/2}^{t+\tau/2} \mathrm{d}t' A(t')$
Volume-average	$\langle A(t) \rangle = \frac{1}{V} \int\limits_{V} \mathrm{d}^3 r A(r,t)$
Ensemble-average	$\langle A(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} A_i(t)$

Table 2: Overview of a few averaging schemes.

The Fluctuation-Dissipation theorem connects the fluctuations in a system with its dissipations. This connection relates the fluctuation correlation function $\langle A'(t) A'(t') \rangle$ with the imaginary part of the response function via the power spectrum being the Fourier transform of the fluctuation correlation function

$$S(\omega) = \frac{1}{\sqrt{2\pi}} \int \mathrm{d}t e^{\mathrm{i}\omega t} \left\langle A'(t) A'(0) \right\rangle . \tag{110}$$

The Fluctuation–Dissipation theorem for a classical field reads

$$S(\omega) = -\frac{2 k_{\mathrm{B}} T}{\omega} \operatorname{Im} \chi(\omega) . \tag{111}$$

Definition 2.2.2

Summary of Dissipation–Fluctuation theorem:
Fluctuations and dissipations go hand in hand: When a system has fluctuations, it automatically dissipates and vice versa. The linear response function of a dissipative system is **always** complex-valued.

As we are dealing with absorbing media, which means that the system absorbs energy (dissipation), we need to introduce noises (fluctuations) to the responses (74)

$$\boldsymbol{P}(\boldsymbol{r}, t) = \varepsilon_0 \int\limits_0^{\infty} \mathrm{d}\tau \chi_{\mathrm{e}}(\boldsymbol{r}, \tau) \boldsymbol{E}(\boldsymbol{r}, t-\tau) + \boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r}, t), \tag{112}$$

with the noise polarisation $\boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r}, t)$ which results from a noise charge density

$$\rho_{\mathrm{N}}(\boldsymbol{r}, \omega) = -\nabla \cdot \boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r}, \omega), \tag{113}$$

and its associated noise charge current density

$$\boldsymbol{j}_{\mathrm{N}}(\boldsymbol{r}, \omega) = -\mathrm{i}\omega \boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r}, \omega) + \nabla \times \boldsymbol{M}_{\mathrm{N}}(\boldsymbol{r}, \omega), \tag{114}$$

with the noise magnetisation $\boldsymbol{M}_{\mathrm{N}}$.

2.2.2 Langevin noise approach

In the absence of free charges and currents, $\varrho_{\text{free}}(\boldsymbol{r},\omega) = 0$ and $\boldsymbol{j}_{\text{free}}(\boldsymbol{r},\omega) = \boldsymbol{0}$, respectively, the electric field is induced by the noise charge current density

$$\boldsymbol{E}(\boldsymbol{r},\omega) = \mathrm{i}\mu_0\omega \int \mathrm{d}^3 r' \mathbf{G}(\boldsymbol{r},\boldsymbol{r}',\omega)\cdot \boldsymbol{j}(\boldsymbol{r}',\omega)\,, \tag{115}$$

where the current is induced by the electric field itself via the generalised Ohm's law

$$\boldsymbol{j}(\boldsymbol{r},\omega) = \int \mathrm{d}^3 r' \mathbf{Q}(\boldsymbol{r},\boldsymbol{r}',\omega)\cdot \boldsymbol{E}(\boldsymbol{r}',\omega) + \boldsymbol{j}_{\mathrm{N}}(\boldsymbol{r},\omega)\,, \tag{116}$$

with the complex conductivity tensor $\mathbf{Q}(\boldsymbol{r},\boldsymbol{r}',\omega)$.
Until this point, all consideration regarding the electromagnetic field regarded classical electrodynamics. To quantise the field, we apply the second quantisation scheme to the noise charge current density as canonical variable $\boldsymbol{j}_{\mathrm{N}} \mapsto \hat{\boldsymbol{j}}_{\mathrm{N}}$. According to this quantisation scheme, we need to calculate the commutator, which we get from the classical Poisson brackets

$$\left\{\boldsymbol{j}_{\mathrm{N}}(\boldsymbol{r},\omega),\boldsymbol{j}^*_{\mathrm{N}}(\boldsymbol{r}',\omega')\right\} \mapsto \frac{1}{\mathrm{i}\hbar}\left[\hat{\boldsymbol{j}}_{\mathrm{N}}(\boldsymbol{r},\omega),\hat{\boldsymbol{j}}^\dagger_{\mathrm{N}}(\boldsymbol{r}',\omega')\right]. \tag{117}$$

The Poisson brackets can be obtained from the Fluctuation–Dissipation theorem according to (116)

$$\left\{\boldsymbol{j}_{\mathrm{N}}(\boldsymbol{r},\omega),\boldsymbol{j}^*_{\mathrm{N}}(\boldsymbol{r}',\omega')\right\} = -\mathrm{i}\frac{\omega}{\pi}\delta(\omega-\omega')\mathrm{Re}\,\mathbf{Q}(\boldsymbol{r},\boldsymbol{r}',\omega)\,, \tag{118}$$

leading the Hamiltonian

$$\hat{H} = \pi\int \mathrm{d}\omega \int \mathrm{d}^3 r \mathrm{d}^3 r'\, \hat{\boldsymbol{j}}^\dagger_{\mathrm{N}}(\boldsymbol{r},\omega)\cdot \mathrm{Re}\,\mathbf{Q}(\boldsymbol{r},\boldsymbol{r}',\omega)\cdot \hat{\boldsymbol{j}}_{\mathrm{N}}(\boldsymbol{r}',\omega)\,. \tag{119}$$

Due to the residual of the commutator, we can conclude that the states $\hat{\boldsymbol{j}}_{\mathrm{N}}(\boldsymbol{r},\omega)$ are not orthogonal. We want to bring the Hamiltonian in the form (63). Introducing the transform

$$\hat{\boldsymbol{f}}(\boldsymbol{r},\omega) = \sqrt{\frac{\hbar\omega}{\pi}}\int \mathrm{d}^3 r' \mathbf{K}(\boldsymbol{r},\boldsymbol{r}',\omega)\cdot \hat{\boldsymbol{j}}_{\mathrm{N}}(\boldsymbol{r}',\omega)\,, \tag{120}$$

we can write the Hamiltonian as

$$\hat{H} = \sum_\lambda \int \mathrm{d}\omega \int \mathrm{d}^3 r\, \hbar\omega\, \hat{\boldsymbol{f}}^\dagger(\boldsymbol{r},\omega)\cdot \hat{\boldsymbol{f}}(\boldsymbol{r},\omega)\,, \tag{121}$$

and the commutator as

$$\left[\hat{\boldsymbol{f}}(\boldsymbol{r},\omega),\hat{\boldsymbol{f}}^\dagger(\boldsymbol{r}',\omega')\right] = \delta(\omega-\omega')\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')\,. \tag{122}$$

But this leaves the question about the transformation matrix $\mathbf{K}(\boldsymbol{r},\boldsymbol{r}',\omega)$. Details about its construction can be found in Ref. [5]. We restrict ourselves to the consideration of spatially local

$$\mathrm{Re}\,\mathbf{Q}(\boldsymbol{r},\boldsymbol{r}',\omega) = \mathrm{Re}\,\mathbf{Q}(\boldsymbol{r},\omega)\delta(\boldsymbol{r}-\boldsymbol{r}')\,, \tag{123}$$

isotropic

$$\mathrm{Re}\,\mathbf{Q}(\boldsymbol{r},\omega) = \mathrm{Re}\,Q(\boldsymbol{r},\omega)\mathbf{1}\,, \tag{124}$$

and inhomogeneous dielectric medium

$$\mathrm{Re}\,Q(\boldsymbol{r},\omega)=\varepsilon_0\omega\mathrm{Im}\chi(\boldsymbol{r},\omega)\,. \tag{125}$$

As **K** is the 'square-root' of the Re **Q**

$$\mathrm{Re}\,\mathbf{Q}(\boldsymbol{r},\boldsymbol{r}',\omega)=\int \mathrm{d}^3s\,\mathbf{K}(\boldsymbol{r},\boldsymbol{s},\omega)\cdot\mathbf{K}^{+}(\boldsymbol{s},\boldsymbol{r}',\omega)\,, \tag{126}$$

we can evaluate it due to the abovementioned assumptions

$$\mathbf{K}(\boldsymbol{r},\boldsymbol{r}',\omega)=\sqrt{\varepsilon_0\omega\mathrm{Im}\chi(\boldsymbol{r},\omega)}\delta(\boldsymbol{r}-\boldsymbol{r}')\mathbf{1}\,. \tag{127}$$

Thus, the electric field operator reads as

$$\hat{\boldsymbol{E}}(\boldsymbol{r},\omega)=\mathrm{i}\sqrt{\frac{\hbar}{\pi\varepsilon_0}}\frac{\omega^2}{c^2}\int \mathrm{d}^3r'\sqrt{\mathrm{Im}\chi(\boldsymbol{r}',\omega)}\mathbf{G}(\boldsymbol{r},\boldsymbol{r}',\omega)\cdot\hat{\boldsymbol{f}}(\boldsymbol{r}',\omega)\,. \tag{128}$$

The ladder operators $\hat{\boldsymbol{f}}$ and $\hat{\boldsymbol{f}}^\dagger$ describe the dressed field excitations meaning photonic excitations **and** media excitations. Therefore, they are often called polaritonic excitations. Some important expectation values are

$$\left\langle\hat{\boldsymbol{f}}(\boldsymbol{r},\omega)\right\rangle=\left\langle\hat{\boldsymbol{f}}^\dagger(\boldsymbol{r},\omega)\right\rangle=\mathbf{0} \tag{129}$$

$$\left\langle\hat{\boldsymbol{f}}(\boldsymbol{r},\omega)\hat{\boldsymbol{f}}(\boldsymbol{r},\omega)\right\rangle=\left\langle\hat{\boldsymbol{f}}^\dagger(\boldsymbol{r},\omega)\hat{\boldsymbol{f}}^\dagger(\boldsymbol{r},\omega)\right\rangle=\mathbf{0} \tag{130}$$

$$\left\langle\hat{\boldsymbol{f}}^\dagger(\boldsymbol{r},\omega)\hat{\boldsymbol{f}}(\boldsymbol{r}',\omega')\right\rangle=n(\omega)\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(\omega-\omega')\mathbf{1}\,, \tag{131}$$

$$\left\langle\hat{\boldsymbol{f}}(\boldsymbol{r},\omega)\hat{\boldsymbol{f}}^\dagger(\boldsymbol{r}',\omega')\right\rangle=(n(\omega)+1)\,\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(\omega-\omega')\mathbf{1}\,, \tag{132}$$

with the averaged thermal photon number

$$n(\omega)=\frac{1}{\mathrm{e}^{\hbar\omega/(k_\mathrm{B}T)}-1}\,. \tag{133}$$

3

SECTION

Dispersion forces

In the previous sections, we looked closer at the treatment of particles with the Hamiltonian (13) and the quantisation of the electromagnetic fields (121). In this section, we want to analyse the coupling between particles and fields via the dipole coupling

$$\hat{H}_{\mathrm{int}} = -\hat{\boldsymbol{d}} \cdot \hat{\boldsymbol{E}} \,. \tag{134}$$

This consideration will guide us to the Casimir–Polder interaction, the interactions between a single particle and a dielectric object, and the van-der-Waals interaction between two polarisable particles.

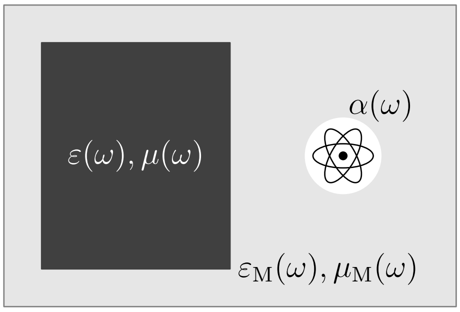

Figure 5: Scatch of the Casimir–Polder interaction: a polarisable particle $\alpha(\omega)$ interacts with an uncharged dielectric object (solid dark grey object) described by the permittivity $\varepsilon(\omega)$ and permeability $\mu(\omega)$.

3.1 The Casimir–Polder potential

The considered scenario is depicted in Fig. 5. Everything surrounding the particle with polarisability $\alpha(\omega)$ (the dielectric object with permeability $\varepsilon(\omega)$ and permittivity $\mu(\omega)$ and the back-ground medium with $\varepsilon(\mathrm{i}\xi)(\omega)$ and $\mu_{\mathrm{M}}(\omega)$) will be considered via the field Hamiltonian $\hat{H}_{\mathrm{F}}$. The particle is described by the Hamiltonian $\hat{H}_{\mathrm{A}}$ (index A for atom). Thus, the combined system is described by unperturbed Hamiltonian

$$\hat{H}_0 = \hat{H}_{\mathrm{F}} + \hat{H}_{\mathrm{A}} \,, \tag{135}$$

leading to the so-called Fock-states $|0,\{\mathbf{0}\}\rangle = |0\rangle\,|\{\mathbf{0}\}\rangle$, as the product of the single states. The total Hamiltonian requires the interaction between both systems

$$\hat{H} = \hat{H}_{\mathrm{F}} + \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{int}}\,. \tag{136}$$

We will solve this equation perturbatively

$$\Delta E = -\,\langle 0,\{\mathbf{0}\}|\,\hat{\boldsymbol{d}}\cdot\hat{\boldsymbol{E}}\,|0,\{\mathbf{0}\}\rangle \tag{137}$$

$$-\sum_k\int \mathrm{d}^3r\,\mathrm{d}\omega\,\frac{\langle 0,\{\mathbf{0}\}|\,\hat{\boldsymbol{d}}\cdot\hat{\boldsymbol{E}}\,|k,\mathbf{1}(\boldsymbol{r},\omega)\rangle\,\langle k,\mathbf{1}(\boldsymbol{r},\omega)|\,\hat{\boldsymbol{d}}\cdot\hat{\boldsymbol{E}}\,|0,\{\mathbf{0}\}\rangle}{\hbar\,(\omega_k-\omega)}+\cdots\,. \tag{138}$$

The first-order vanishes due to Eq. (129). Similar to the cancellation for the field operators, one can apply the selection rules for the dipole operator, which only captures transition dipole moments. Transitions are from one state to another. As the initial and final state are both the ground state, we do not find any transition. By writing the excited field state as an excitation of the ground-state

$$\hat{\boldsymbol{f}}^{\dagger}(\boldsymbol{r},\omega)\,|\{\mathbf{0}\}\rangle = |\mathbf{1}(\boldsymbol{r},\omega)\rangle\;, \tag{139}$$

we can evaluate the matrix element

$$\begin{aligned}\langle k,\mathbf{1}(\boldsymbol{r},\omega)|\,\hat{\boldsymbol{d}}\cdot\hat{\boldsymbol{E}}(\boldsymbol{r}_A)\,|0,\{\{\mathbf{0}\}\rangle &= \langle k|\,\hat{\boldsymbol{d}}\,|0\rangle\,\langle\{\mathbf{0}\}|\,\hat{\boldsymbol{f}}(\boldsymbol{r},\omega)\hat{\boldsymbol{E}}(\boldsymbol{r}_A)\,|\{\mathbf{0}\}\rangle\\ &= \boldsymbol{d}_{k0}\cdot\mathbf{G}^{*,T}(\boldsymbol{r}_A,\boldsymbol{r},\omega)\,,\end{aligned} \tag{140}$$

where we applied Eq. (132). The remaining term in the nominator of Eq. (138) is its complex-conjugated and transposed result. Together with the integral relation for Green functions

$$\int \mathrm{d}^3s\,\mathbf{G}(\boldsymbol{r},\boldsymbol{s},\omega)\cdot\mathbf{G}^{*,T}(\boldsymbol{s},\boldsymbol{r}',\omega) = \frac{\hbar\mu_0}{\pi}\omega^2\,\mathrm{Im}\,\mathbf{G}(\boldsymbol{r},\boldsymbol{r}',\omega)\,, \tag{141}$$

we find the energy shift

$$\Delta E = -\sum_k\int\frac{\mathrm{d}\omega\,\mu_0\omega^2}{\pi(\omega_k-\omega)}\boldsymbol{d}_{0k}\cdot\mathrm{Im}\,\mathbf{G}(\boldsymbol{r}_A,\boldsymbol{r}_A,\omega)\cdot\boldsymbol{d}_{k0}\,, \tag{142}$$

leading to the interpretation that the Casimir–Polder potential is proportional to the optical local-mode density $\mathrm{Im}\,\mathbf{G}(\boldsymbol{r}_A,\boldsymbol{r}_A,\omega)$. Recalling the separation of the Green function into its bulk and scattering part (89), we can split the result into position-dependent part

$$\Delta E = -\sum_k\int\frac{\mathrm{d}\omega\,\mu_0\omega^2}{\pi(\omega_k-\omega)}\boldsymbol{d}_{0k}\cdot\mathrm{Im}\,\mathbf{G}^{(S)}(\boldsymbol{r}_A,\boldsymbol{r}_A,\omega)\cdot\boldsymbol{d}_{k0}\,, \tag{143}$$

and a position-independent part

$$\Delta E = -\sum_k\int\frac{\mathrm{d}\omega\,\mu_0\omega^2}{\pi(\omega_k-\omega)}\boldsymbol{d}_{0k}\cdot\mathrm{Im}\,\mathbf{G}^{(0)}(\boldsymbol{r}_A,\boldsymbol{r}_A,\omega)\cdot\boldsymbol{d}_{k0}\,. \tag{144}$$

The latter can be evaluated explicitly by inserting the free-space Green function (98) leading to the Lamb shift

$$\Delta E_{\mathrm{Lamb}} = \frac{\mu_0}{6\pi^2c}\sum_k\omega_k^3|\boldsymbol{d}_{0k}|^2\ln\left(\frac{m_ec^2}{\hbar\omega_k}\right)\,. \tag{145}$$

The position-dependent contribution is the Casimir–Polder potential, which can be manipulated further by using $\mathrm{Im}\mathbf{G} = (\mathbf{G}-\mathbf{G}^*)/(2\mathrm{i})$ and Schwarz reflection principle $\mathbf{G}^*(\omega) = \mathbf{G}(-\omega^*)$ leading

$$U_{\mathrm{CP}}(\boldsymbol{r}_A) = \frac{\mu_0}{2i\pi}\sum_k \left[\int\limits_0^{\infty} \frac{\mathrm{d}\omega}{\omega_k+\omega} - \int\limits_0^{-\infty} \frac{\mathrm{d}\omega}{\omega_k-\omega}\right] \omega_k \omega \boldsymbol{d}_{0k}\cdot \mathbf{G}^{(S)}(\boldsymbol{r}_A,\boldsymbol{r}_A,\omega)\cdot \boldsymbol{d}_{k0}\,. \tag{146}$$

These integrals can be flipped to the imaginary frequency axis by applying contour integral techniques. The Green function is a so-called holomorphic function, meaning it has no divergencies in the upper complex half-plane. Thus, the integration along a closed contour in the upper half-plane always vanishes

$$\oint \mathbf{G}(\boldsymbol{r},\boldsymbol{r},\omega)\mathrm{d}\omega = 0\,. \tag{147}$$

By choosing the integration paths as depicted in Fig. 6,

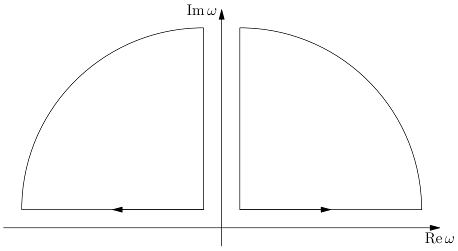

Figure 6: Contours for integrating the Casimir–Polder potential to flip from real to imaginary frequencies.

1st path: along the positive real frequency axis, followed by the angle from 0 to $\pi/2$ along the infinite line and going back along the imaginary axis

2nd path: along the negative real frequency axis, continued via the infinite line over the angle from π to $\pi/2$, and again going back along the imaginary axis,

both integrals can be turned onto the imaginary frequency axis, leading to

$$U_{\mathrm{CP}}(\boldsymbol{r}_A) = \frac{\mu_0}{\pi}\sum_k \int\limits_0^{\infty} \mathrm{d}\xi \frac{\omega_k \xi^2}{\omega_k^2+\xi^2}\mathbf{d}_{0k}\cdot \mathbf{G}^{(S)}(\boldsymbol{r}_A,\boldsymbol{r}_A,\mathrm{i}\xi)\cdot \mathbf{d}_{k0}\,. \tag{148}$$

At the beginning of this chapter, we mentioned the interaction between a polarisable particle and a dielectric object. Hence, the final step is to convert the transition dipole moments to the ground-state polarisability via

$$\boldsymbol{\alpha}(\omega) = \lim_{\epsilon\to 0+}\frac{1}{\hbar}\sum_k \left(\frac{\boldsymbol{d}_{k0}\boldsymbol{d}_{0k}}{\omega+\omega_k+\mathrm{i}\epsilon} - \frac{\boldsymbol{d}_{0k}\boldsymbol{d}_{k0}}{\omega-\omega_k+\mathrm{i}\epsilon}\right) \tag{149}$$

By using the relation $\boldsymbol{a}\cdot\mathbf{A}\cdot\boldsymbol{b} = a_i A_{ij} b_j = b_j a_i A_{ij} = \mathrm{tr}[(\boldsymbol{b}\boldsymbol{a})\cdot\mathbf{A}]$, we find the Casimir–Polder potential

$$U_{\mathrm{CP}}(\boldsymbol{r}_A) = \frac{\hbar\mu_0}{2\pi}\int\limits_0^{\infty} \mathrm{d}\xi\,\xi^2\,\mathrm{tr}\left[\boldsymbol{\alpha}(\mathrm{i}\xi)\cdot\mathbf{G}^{(S)}(\boldsymbol{r}_A,\boldsymbol{r}_A,\mathrm{i}\xi)\right]. \tag{150}$$

In contrast to the previous result (142), this equation (150) contains the entire scattering Green function instead of its imaginary part. In this sense, we can interpret the Casimir–Polder potential as an exchange of virtual photons. The Green function is the field propagator for classical fields and the photon propagator for quantised fields. The ground-state fluctuations of the electromagnetic field spontaneously create a virtual photon at the particle's position. This virtual photon is emitted into the entire space, reflected at the surrounding interfaces and propagates back to the particle (equal position arguments in the Green function, $\mathbf{G}(\boldsymbol{r}_A, \boldsymbol{r}_A, \omega)$, also called coincidence limit). The virtual photon interacts with the particle by reaching the particle, expressed by the polarisability. These vacuum fluctuations occur at all frequencies. For this reason, we have to sum (integrate) over all frequencies. A virtual photon is a quasi-particle, meaning it does not exist freely. It only appears for interactions with other objects. But it behaves like real photons and thus can be manipulated like a real photon. These manipulations are, for instance, reflections at interfaces or absorption by media.

3.2 An atom in front of an infinite half-space

In the case of an atom in front of an infinite half-space, we need the Green function to reflect an electromagnetic wave at a single interface. The corresponding Green function can be calculated analytically and reads for an interface located in the $z = 0$-plane

$$\mathbf{G}^{(S)}_{\mathrm{pl}}(\boldsymbol{r}, \boldsymbol{r}', \omega) = \frac{\mathrm{i}}{8\pi^2} \int \frac{\mathrm{d}^2 k^{\parallel}}{k_1^{\perp}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}^{\parallel}\cdot(\boldsymbol{r}-\boldsymbol{r}')+\mathrm{i}k_1^{\perp}(z+z')} \left[r_s \boldsymbol{e}^1_{s+} \boldsymbol{e}^1_{s-} + r_p \boldsymbol{e}^1_{p+} \boldsymbol{e}^1_{p-} \right], \tag{151}$$

with the Fresnel reflection coefficients for s-polarised waves

$$r_s = \frac{k_1^{\perp} - k_2^{\perp}}{k_1^{\perp} + k_2^{\perp}}, \tag{152}$$

and for p-polarised waves

$$r_p = \frac{\varepsilon_2 k_1^{\perp} - \varepsilon_1 k_2^{\perp}}{\varepsilon_2 k_1^{\perp} + \varepsilon_1 k_2^{\perp}}, \tag{153}$$

and the corresponding polarisation unit vector $\boldsymbol{e}_{s,p,\pm}$. The indices at perpendicular wave vectors and the superscripts at the polarisation vectors indicate the region (medium). They are 1 for $z > 0$ and 2 for $z < 0$. The parallel wave vector is parallel to the plane $\boldsymbol{k}^{\parallel} \perp \boldsymbol{e}_z$. The z-component of the wave vector reads

$$k_j^{\perp} = \sqrt{\varepsilon_j \frac{\omega^2}{c^2} - k^{\parallel 2}}. \tag{154}$$

By introducing spherical coordinates for the $\boldsymbol{k}^{\parallel}$ integral, $\boldsymbol{k} = k^{\parallel}(\cos\varphi, \sin\varphi, 0)$, one finds

$$\boldsymbol{e}^j_{s\pm} = \boldsymbol{e}_{k^{\parallel}} \times \boldsymbol{e}_z = (\sin\varphi, -\cos\varphi, 0), \tag{155}$$

and

$$\boldsymbol{e}^j = \frac{1}{k_j}\left(k^{\parallel}\boldsymbol{e}_z \mp k_j^{\perp}\boldsymbol{e}_{k^{\parallel}}\right) = \frac{c}{\omega\sqrt{\varepsilon_j}}(\mp k_j^{\perp}\cos\varphi, \mp k_j^{\perp}\sin\varphi, k^{\parallel}). \tag{156}$$

Thus, the dyads in Eq. (151) read

$$\boldsymbol{e}^1_{s+}\boldsymbol{e}^1_{s-} = \begin{pmatrix} \sin^2\varphi & -\sin\varphi\cos\varphi & 0 \\ -\sin\varphi\cos\varphi & \cos^2\varphi & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{157}$$

and

$$\boldsymbol{e}^1_{p+}\boldsymbol{e}^1_{p-} = -\frac{c^2}{\omega^2\varepsilon_1}\begin{pmatrix} {k_1^\perp}^2\cos^2\varphi & {k_1^\perp}^2\sin\varphi\cos\varphi & -k^\parallel k_1^\perp\cos\varphi \\ {k_1^\perp}^2\sin\varphi\cos\varphi & {k_1^\perp}^2\sin^2\varphi & -k^\parallel k_1^\perp\sin\varphi \\ k^\parallel k_1^\perp\cos\varphi & k^\parallel k_1^\perp\sin\varphi & -{k^\parallel}^2 \end{pmatrix}, \tag{158}$$

and the angular integral can be carried out. As the Casimir–Polder potential (150) lives on the imaginary frequency axis, we need to substitute $\omega = \mathrm{i}\xi$, and we observe that the perpendicular wave vector turns purely imaginary

$$k_j^\perp = \sqrt{\varepsilon_j\frac{\omega^2}{c^2} - {k^\parallel}^2} = \sqrt{-\varepsilon_j\frac{\xi^2}{c^2} - {k^\parallel}^2} = \mathrm{i}\sqrt{\varepsilon_j\frac{\xi^2}{c^2} + {k^\parallel}^2} = \mathrm{i}\kappa_j\,, \tag{159}$$

and we call its imaginary part κ_j. Consequently, the reflection coefficients turn real

$$r_s = \frac{\kappa_1^\perp - \kappa_2^\perp}{\kappa_1^\perp + \kappa_2^\perp}\,, \qquad r_p = \frac{\varepsilon_2\kappa_1^\perp - \varepsilon_1\kappa_2^\perp}{\varepsilon_2\kappa_1^\perp + \varepsilon_1\kappa_2^\perp}\,. \tag{160}$$

By applying the coincidence limit $\boldsymbol{r}' \mapsto \boldsymbol{r}$, the Green function gets exponentially damped (evanescence waves). Finally, the Green function reads

$$\mathbf{G}^{(S)}_{\mathrm{pl}}(\boldsymbol{r}_A, \boldsymbol{r}_A, \mathrm{i}\xi) = \frac{1}{8\pi}\int_0^\infty \frac{k^\parallel \mathrm{d}k^\parallel}{\kappa_1}\mathrm{e}^{-2\kappa_1 z}\left[r_s\begin{pmatrix}1&0&0\\0&1&0\\0&0&0\end{pmatrix} - \frac{r_p c^2}{\xi^2\varepsilon_1}\begin{pmatrix}\kappa_1^2&0&0\\0&\kappa_1^2&0\\0&0&2{k^\parallel}^2\end{pmatrix}\right]. \tag{161}$$

Inserting this result into the Casimir–Polder potential (150), assuming an isotropic particle $\boldsymbol{\alpha} = \alpha\mathbf{1}$ located in vacuum $\varepsilon_1 = 1$, we find the Casimir–Polder potential

$$U_{\mathrm{CP}}(z_A) = \frac{\hbar\mu_0}{8\pi^2}\int_0^\infty \mathrm{d}\xi\,\xi^2\alpha(\mathrm{i}\xi)\int_{\xi/c}^\infty \mathrm{d}\kappa\mathrm{e}^{-2\kappa z_A}\left[\frac{\kappa-\kappa_2}{\kappa+\kappa_2} + \left(1 - 2\frac{\kappa^2c^2}{\xi^2}\right)\frac{\varepsilon(\mathrm{i}\xi)\kappa-\kappa_2}{\varepsilon(\mathrm{i}\xi)\kappa+\kappa_2}\right], \tag{162}$$

with the imaginary part of the wave vector in the second medium

$$\kappa_2 = \sqrt{[\varepsilon(\mathrm{i}\xi) - 1]\frac{\xi^2}{c^2} + \kappa^2}\,. \tag{163}$$

In the non-retarded limit, when the distance between the atom and the interface is much smaller than the dominant wavelengths $z_A \ll c/\bar{\omega}$. Thus, the dominant contribution to the integral arises from large wave vectors due to the exponential function. For this reason, we can approximate the perpendicular wave vectors to be equal

$$\kappa_2 \approx \kappa\,, \tag{164}$$

leading to the cancellation of the reflection coefficient for s-polarised waves, $r_s = 0$ and the reflection coefficient for p-polarised waves becomes κ-independent

$$U_{\mathrm{CP}}(z_A) = -\frac{\hbar}{4\pi^2\varepsilon_0}\int_0^\infty \mathrm{d}\xi\,\alpha(\mathrm{i}\xi)\frac{\varepsilon(\mathrm{i}\xi)-1}{\varepsilon(\mathrm{i}\xi)+1}\int_{\xi/c}^\infty \mathrm{d}\kappa\,\kappa^2\mathrm{e}^{-2\kappa z_A}\,. \tag{165}$$

By shifting the lower bound of the remaining integral to 0, the integral can be carried out analytically and results in the well-known C_3-potential

$$U_{\mathrm{CP}}(z_A) = -\frac{C_3}{z_A^3}\,, \tag{166}$$

with

$$C_3 = \frac{\hbar}{16\pi^2\varepsilon_0}\int_0^\infty \mathrm{d}\xi\,\alpha(\mathrm{i}\xi)\frac{\varepsilon(\mathrm{i}\xi)-1}{\varepsilon(\mathrm{i}\xi)+1}\,. \tag{167}$$

In contrast, for larger separations $z_A \gg c/\bar{\omega}$, we can restrict the frequency integral to be dominated by its static contributions, leading to the C_4-potential

$$U_{\mathrm{CP}}(z_A) = -\frac{C_4}{z_A^4}\,, \tag{168}$$

with

$$C_4 = \frac{3\hbar c\alpha(0)}{64\pi^2\varepsilon_0}\int_1^\infty \mathrm{d}v\left[\left(\frac{2}{v^2}-\frac{1}{v^4}\right)\frac{\varepsilon(0)\,v-\sqrt{(v^2-1)+\varepsilon(0)}}{\varepsilon(0)\,v+\sqrt{(v^2-1)+\varepsilon(0)}}-\frac{1}{v^4}\frac{v-\sqrt{(v^2-1)+\varepsilon(0)}}{v+\sqrt{(v^2-1)+\varepsilon(0)}}\right]. \tag{169}$$

The different approximations are depicted in Fig. 7. It can be observed that the non-retarded approximation is only valid for separations smaller than 10 nm. The retarded potential has a small deviation concerning the exact solution, which is caused by temperature. The largest deviation of both approximations is around 100 nm.

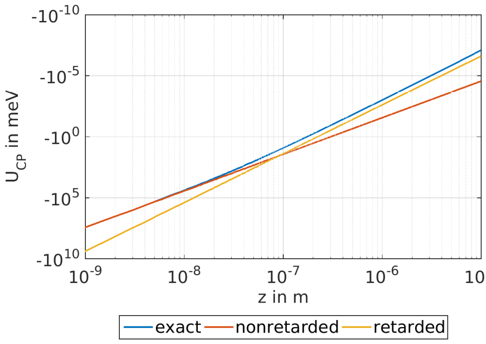

Figure 7: Casimir–Polder potential for an atom in front of an infinite half-space: exact solution (Eq. (43); blue line), retarded potential (Eq. (168); yellow line) and non-retarded potential (Eq. (166); red line).

3.3 Born Series expansion

In the previous chapters, we derived the Casimir–Polder potential in terms of field propagators (Green function of the vector Helmholtz equation). We applied the theory to the simple case of an atom in front of an infinite half-space. The Green functions are analytically known for planarly, cylindrically and spherically layered systems. Furthermore, the solution in orthogonal elliptical coordinates exists. However, most of the interesting scenarios have other geometries. For this reason, one needs to find ways to approximate the scattering Green function for arbitrary geometries. Beyond numerical solutions, for instance, calculating the mode structure via COMSOL or calculating surface currents via scuff-em, approximation methods exist. For instance, by combining known geometries, such as two cylinders or a sphere and a plane, one usually applies mode-matching techniques that develop the Green function of one object in the shifted basis of the others. For periodic structures, one often uses the Rayleigh series expansion. This expansion develops the field in plane waves and obtains effective reflection and transmission coefficients for each mode.

In arbitrary geometries, the Born series expansion is typically the method of choice.

We are interested in the solution of the vector Helmholtz equation for a given system represented by the spatial dielectric function

$$\left[\nabla\times\nabla\times-\frac{\omega^2}{c^2}\varepsilon(\boldsymbol{r},\omega)\right]\mathbf{G}(\boldsymbol{r},\boldsymbol{r}',\omega)=\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')\,. \quad (170)$$

To solve this system, we introduce a reference Green tensor satisfying the Helmholtz equation (bulk, vacuum, layered media, ...)

$$\left[\nabla\times\nabla\times-\frac{\omega^2}{c^2}\varepsilon_0(\boldsymbol{r},\omega)\right]\mathbf{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega)=\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')\,. \quad (171)$$

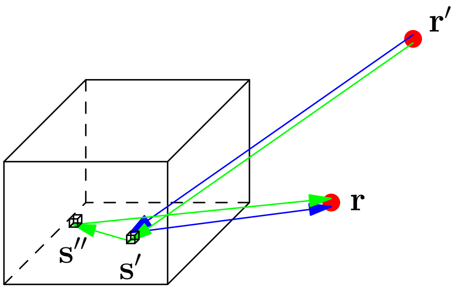

Figure 8: Sketch of the Born series expansion for the scattering at a cube.

One typically uses the bulk Green function and, on molecular, atomic or even subatomic scales, the vacuum Green function. Calculating the difference between both equations yields

$$\left[\nabla\times\nabla\times-\frac{\omega^2}{c^2}\varepsilon_0(\boldsymbol{r})\right]\mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}')=\frac{\omega^2}{c^2}\delta\varepsilon\left[\mathbf{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')+\mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}')\right], \quad (172)$$

with the difference dielectric function

$$\delta\varepsilon=\delta\varepsilon(\boldsymbol{r},\omega)=\varepsilon(\boldsymbol{r},\omega)-\varepsilon_0(\boldsymbol{r},\omega)\,. \quad (173)$$

Thus, equation (172) shows that the wanted Green function $\mathbf{G}^{(S)}$ is induced by the reference Green function $\mathbf{G}^{(0)}$ with the inhomogeneity

$$\frac{\omega^2}{c^2}\delta\varepsilon\left[\mathbf{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')+\mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}')\right]. \quad (174)$$

Finally, we can write its solution formally as a convolution of the fundamental solution with the inhomogeneity

$$\mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}',\omega)=\int \mathrm{d}^3s\,\mathbf{G}^{(0)}(\boldsymbol{r},\mathbf{s},\omega)\cdot\frac{\omega^2}{c^2}\delta\varepsilon\left[\mathbf{G}^{(0)}(\mathbf{s},\boldsymbol{r}',\omega)+\mathbf{G}^{(S)}(\mathbf{s},\boldsymbol{r}',\omega)\right]. \quad (175)$$

The resulting integral equation is typically solved iteratively. Its first-order term is given by neglecting the scattering Green function in the integrant

$$\mathbf{G}_1^{(S)}(\boldsymbol{r},\boldsymbol{r}',\omega)=\int \mathrm{d}^3s\,\mathbf{G}^{(0)}(\boldsymbol{r},\mathbf{s},\omega)\cdot\frac{\omega^2}{c^2}\delta\varepsilon\mathbf{G}^{(0)}(\mathbf{s},\boldsymbol{r}',\omega)\,. \quad (176)$$

The next order can be obtained by plugging in the result of the first order in the integrant

$$\mathbf{G}_2^{(S)}(\boldsymbol{r},\boldsymbol{r}',\omega)=\int \mathrm{d}^3s\,\mathbf{G}^{(0)}(\boldsymbol{r},\mathbf{s},\omega)\cdot\frac{\omega^2}{c^2}\delta\varepsilon\left[\mathbf{G}^{(0)}(\mathbf{s},\boldsymbol{r}',\omega)+\mathbf{G}_1^{(S)}(\mathbf{s},\boldsymbol{r}',\omega)\right], \quad (177)$$

and so on. This series expansion is equivalent to the Dyson series in Quantum Field Theory. The free-space Green function is typically considered in the Born series expansion, illustrated in Fig. 8. The scattering from the source point $\boldsymbol{r}'$ to the final point rr is expanded in terms of scattering events. The first order means that a single volume element at $\boldsymbol{s}'$ of the dielectric body scatter each photon

$$\mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}',\omega)=\frac{\omega^2}{c^2}\int \mathrm{d}^3s'\mathbf{G}^{(0)}(\boldsymbol{r},\boldsymbol{s}',\omega)\cdot\delta\varepsilon(\boldsymbol{s}',\omega)\cdot\mathbf{G}^{(0)}(\boldsymbol{s}',\boldsymbol{r}',\omega)\,. \quad (178)$$

In terms of dispersion forces, this approximation is known as Hamaker approach (pairwise summation when $\boldsymbol{r}' \mapsto \boldsymbol{r}$). The second order considers a further scattering event inside the dielectric body

$$\mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}') = \left(\frac{\omega^2}{c^2}\right)^2 \int \mathrm{d}^3s'\mathrm{d}^3s''\mathbf{G}^{(0)}(\boldsymbol{r},\boldsymbol{s}')\cdot\delta\varepsilon(\boldsymbol{s}')\cdot\mathbf{G}^{(0)}(\boldsymbol{s}',\boldsymbol{s}'')\cdot\delta\varepsilon(\boldsymbol{s}'')\cdot\mathbf{G}^{(0)}(\boldsymbol{s}'',\boldsymbol{r}')\,. \tag{179}$$

As illustrated in Fig. 8, the second order of the Born series expansion considers three-body effects (Axilrod–Teller interactions).

In sec. 2.1.3, we considered the bulk Green function and observed that the Green function consists of two parts: a regular part $\mathbf{R}$ describing the propagation of the photons and a singular part $\boldsymbol{\delta}$ leading to the self-energy of the particles. Thus, we can apply a singularity extraction to the Green function

$$\mathbf{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \lambda\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}') + \mathbf{R}(\boldsymbol{r},\boldsymbol{r}',\omega)\,, \tag{180}$$

with $\lambda = -c^2/(3\omega^2)$ for vacuum. The incoming and outgoing photons, described by the outer Green functions, are regular. But all remaining Green functions for all orders include the self-energies when the internal scattering points meet each other. Thus, we can correct the first order by including the self-energies from the higher orders, leading to

$$\mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{\omega^2}{c^2}\delta\varepsilon(\omega)\int \mathrm{d}^3s \sum_{i=0}^{\infty}\left[\frac{\omega^2}{c^2}\lambda\delta\varepsilon\right]^i \mathbf{R}(\boldsymbol{r},\boldsymbol{s},\omega)\cdot\mathbf{R}(\boldsymbol{s},\boldsymbol{r}',\omega)\,. \tag{181}$$

The sum can be identified as a geometric series and, thus, can be carried out

$$\sum_{i=0}^{\infty}\left[\frac{\omega^2}{c^2}\lambda\delta\varepsilon\right]^i = \left(1-\left[\frac{\omega^2}{c^2}\lambda\delta\varepsilon\right]\right)^{-1}, \tag{182}$$

and yields the local-field corrected Green function

$$\mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{\omega^2}{c^2}\frac{\chi(\omega)}{1+\chi(\omega)/3}\int \mathrm{d}^3s\mathbf{R}(\boldsymbol{r},\boldsymbol{s},\omega)\cdot\mathbf{R}(\boldsymbol{s},\boldsymbol{r}',\omega)\,, \tag{183}$$

with $\chi(\omega) = \varepsilon(\omega) - 1$.

3.4 Van-der-Waals potential

The van-der-Waals force acts between two polarisable particles. One is located at $\boldsymbol{r}_A$ with polarisability α_A and the other at $\boldsymbol{r}_B$ with polarisability α_B. The common procedure to derive the van-der-Waals potential in analogy to the Casimir–Polder potential3.1 would be to apply perturbation theory to the interaction Hamiltonian

$$H_{\mathrm{int}} = -\hat{\boldsymbol{d}}_A\cdot\hat{\boldsymbol{E}}(\boldsymbol{r}_A) - \hat{\boldsymbol{d}}_B\cdot\hat{\boldsymbol{E}}(\boldsymbol{r}_B)\,. \tag{184}$$

Its first three orders will vanish due to the selection rules; thus, we need to consider the fourth order of the perturbation series. This yields a very long calculation [5]. Instead, we can start with the Casimir–Polder potential (150) and consider the scattering at a single point $\boldsymbol{r}_B$. Let's look closely at the coefficient we derived in the previous section in equation (183)

$$\frac{\chi(\omega)}{1+\chi(\omega)/3} = 3\frac{\varepsilon-1}{\varepsilon+2}\,, \tag{185}$$

which is equivalent to the Clausius–Mossotti relation

$$3\frac{\varepsilon-1}{\varepsilon+2} = \frac{\alpha}{\varepsilon_0}\,. \tag{186}$$

Thus, by considering the scattering at a single point $\boldsymbol{r}_B$, the integral reduces to

$$\mathbf{G}^{(S)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{\omega^2}{\varepsilon_0 c^2}\alpha_B(\omega)\mathbf{R}(\boldsymbol{r},\boldsymbol{r}_B,\omega)\cdot\mathbf{R}(\boldsymbol{r}_B,\boldsymbol{r}',\omega)\,. \tag{187}$$

By plugging this result into the Casimir–Polder potential, we end up with the van-der-Waals potential

$$U_{\mathrm{vdW}}(\boldsymbol{r}_A,\boldsymbol{r}_B) = -\frac{\hbar\mu_0^2}{2\pi}\int\limits_0^\infty \mathrm{d}\xi\,\xi^4\,\mathrm{tr}\left[\boldsymbol{\alpha}_A(\mathrm{i}\xi)\cdot\mathbf{G}(\boldsymbol{r}_A,\boldsymbol{r}_B,\mathrm{i}\xi)\cdot\boldsymbol{\alpha}_B(i\xi)\cdot\mathbf{G}(\boldsymbol{r}_B,\boldsymbol{r}_A,\mathrm{i}\xi)\right]\,, \tag{188}$$

where we used that $\boldsymbol{r}_A \neq \boldsymbol{r}_B$ to include to general Green function. We can interpret this result again via an exchange of virtual photons. Caused by the ground-state fluctuations of the electromagnetic field, a virtual photon is created at the position of particle *A*, which propagates to particle *B*. Here, it interacts with this particle (α_B) before returning to particle *A* and interacting with it. The sum (integral) of all these virtual photon exchanges yields the van-der-Waals potential.

3.5 Van-der-Waals interactions in free space

In section 2.1.3, we calculated the free-space Green function. Considering two isotropic particles, $\boldsymbol{\alpha}_{A,B} = \alpha_{A,B}\mathbf{1}$, separated by the distance ϱ, then the trace over the remaining Green functions can be carried out, and the van-der-Waals potential reads

$$U_{\mathrm{vdW}}(\varrho) = -\frac{\hbar}{16\pi^3\varepsilon_0^2\varrho^6}\int\limits_0^\infty \mathrm{d}\xi\,\alpha_A(\mathrm{i}\xi)\alpha_B(\mathrm{i}\xi)g\left(\frac{\xi\varrho}{c}\right)\,, \tag{189}$$

with

$$g(x) = \left(3+6x+5x^2+2x^3+x^4\right)\mathrm{e}^{-2x}\,. \tag{190}$$

Analogously to the Casimir–Polder potential, we can approximate the van-der-Waals potential concerning the relevant length scale. In the non-retarded limit, where the separation is much smaller than the relevant wavelength, $\varrho \ll c/\omega$, the polarisability restricts the integral to a region where $g(\xi\varrho/c) \approx g(0) = 3$, leading to the well-known c_6 potential

$$U_{\mathrm{vdW}}(\varrho) = -\frac{C_6}{\varrho}\,, \qquad C_6 = \frac{3}{16\pi^3\varepsilon_0^2}\int\limits_0^\infty \mathrm{d}\xi\,\alpha_A(\mathrm{i}\xi)\alpha_B(\mathrm{i}\xi)\,. \tag{191}$$

In contrast, for larger separations, the dominant part of the frequency integral is restricted to the electrostatic contributions, and we can carry out the remaining integral

$$\int\limits_0^\infty \mathrm{d}\xi\, g\left(\frac{\xi\varrho}{c}\right) = \frac{c}{\varrho}\int\limits_0^\infty \mathrm{d}x\, g(x) = \frac{23}{4}\frac{c}{\varrho}\,, \tag{192}$$

leading to the retarded van-der-Waals potential

$$U_{\mathrm{vdW}}(\varrho) = -\frac{C_7}{\varrho^7}\,, \qquad C_7 = \frac{23\hbar c\alpha_A\alpha_B}{64\pi^3\varepsilon_0^2}\,. \tag{193}$$

These results are the simple free-space van-der-Waals potentials. If the particles are embedded in a dielectric medium, these potentials need to be adapted concerning the screening effects due to the absorption of photon energy bypassing the medium. The access (or effective) polarisability models, see Ref. [6], considers a vacuum layer surrounding the particles and compensate for its impact on the exchange of virtual photons. This is a local-field effect. Considering the interaction between two dissolved particles, one often speaks about effective screening models; see Ref. [7] for further details.

SECTION 4

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