The origin of van-der-Waals forces

Fundamental concepts and their consequences

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UNIVERSITY OF BERGEN

Acknowledgements

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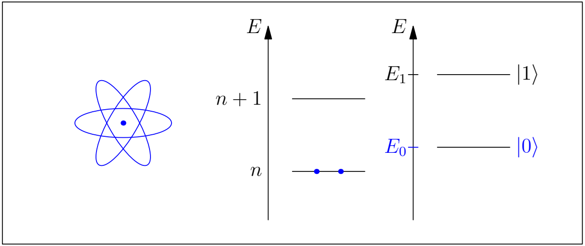

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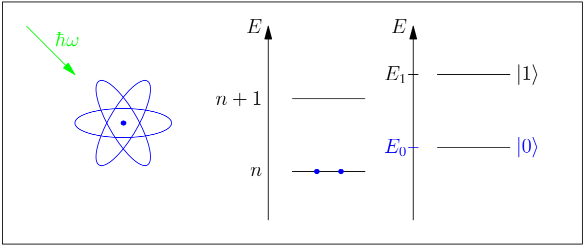

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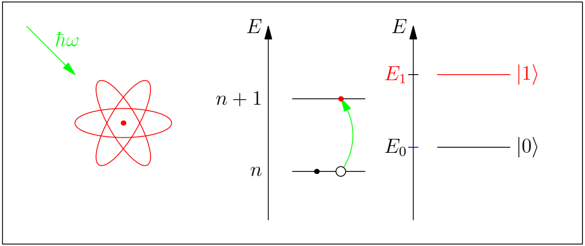

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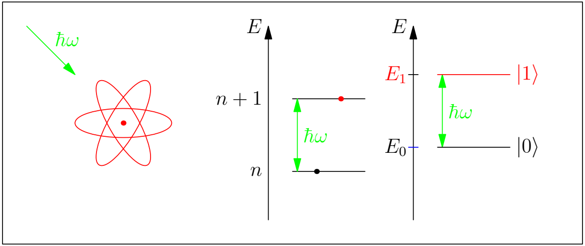

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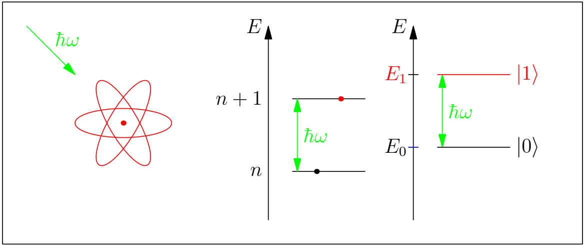

- Moved one electron one level up $n \to n + 1$

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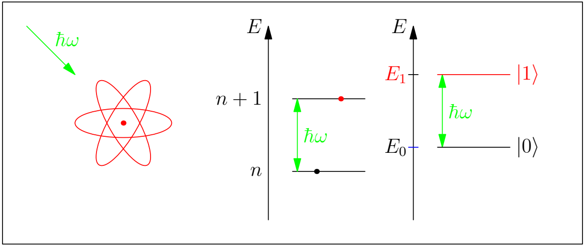

- Moved one electron one level up $n \to n+1$
- Displaced a charge e by distance $a_0^*\,(2n+1)$ (a_0^* reduced Bohr radius)

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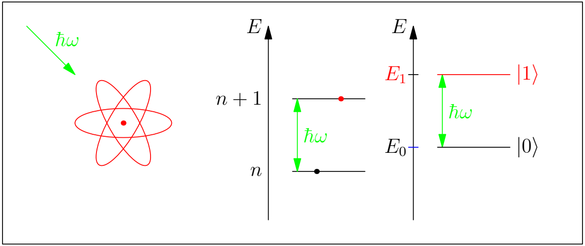

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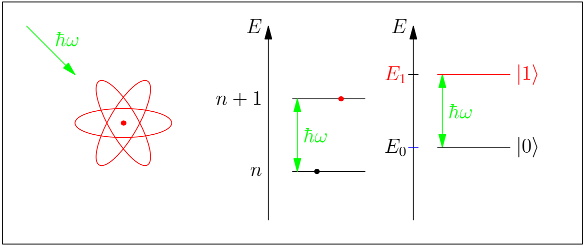

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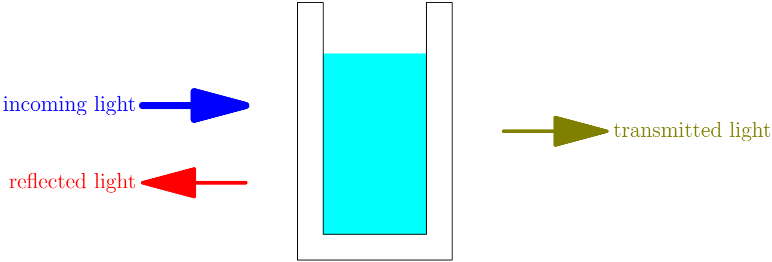
- Laser described by electric field

$$\boldsymbol{d} = \boldsymbol{\alpha} \cdot \boldsymbol{E}$$

with polarisability tensor $\boldsymbol{\alpha}$

Measuring media's responses



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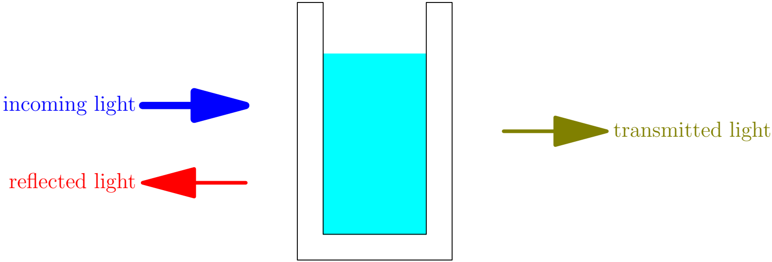
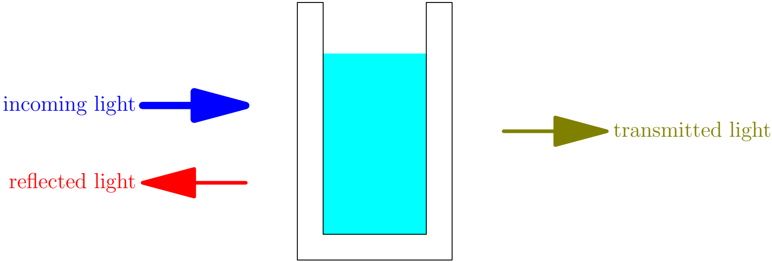


- Reflected light (red) $\rightarrow$ refractive index n

Measuring media's responses



- Reflected light (red) $\rightarrow$ refractive index n
- Transmitted light (green) $\rightarrow$ extinction coefficient κ

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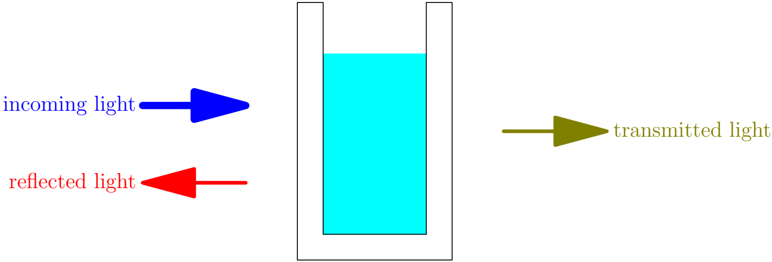

- Reflected light (red) $\rightarrow$ refractive index n
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- Both quantities are combined into the complex dielectric function

$$\varepsilon(\omega) = (n + i\kappa)^2$$

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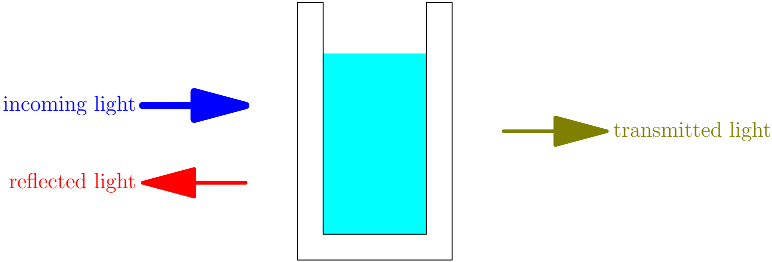

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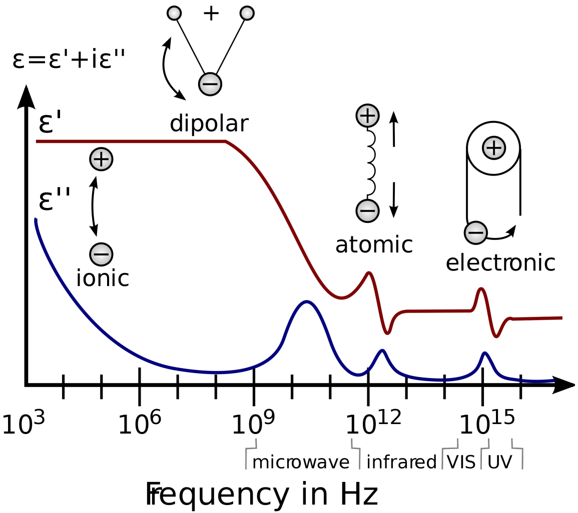
Propagation of a wave: $\varphi(r) = \mathrm{e}^{ik\sqrt{\varepsilon}r} = \mathrm{e}^{ikn(\omega)r}\mathrm{e}^{-k\kappa(\omega)r}$

Dielectric functions as fingerprint of matter



Polarisability vs. Permittivity

Clausius–Mossotti relation

$$\alpha(\omega) = 3V\varepsilon_0 \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 2}$$

Polarisability

Permittivity

Polarisability vs. Permittivity

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Polarisability

- Microscopic quantity

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- Independent on system size
- Upscaling to the macroscopic system

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- **Extensive quantity**

Permittivity

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- Independent on system size
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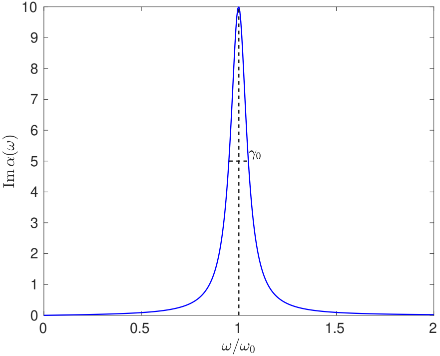
- **Intensive quantity**

Particle's polarisability

$$\alpha_0(\omega) = \sum_j \frac{c_{0j}}{\omega_{0j}^2 - \omega^2 - i\gamma_{j0}\omega}$$



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$$\alpha_0(\omega) = \sum_j \frac{c_{0j}}{\omega_{0j}^2 - \omega^2 - i\gamma_{j0}\omega}$$

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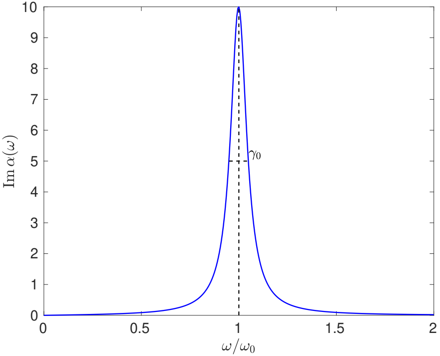
  $\omega_{0j} = \frac{1}{\hbar}\left[\langle j|\,\hat{\mathrm{H}}_\mathrm{A}\,|j\rangle - \langle 0|\,\hat{\mathrm{H}}_\mathrm{A}\,|0\rangle\right]$



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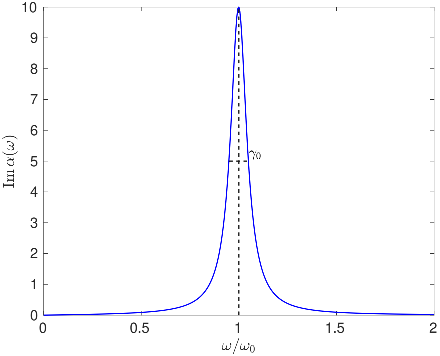
- Amplitude
  $c_{0j} = \frac{2\left|\boldsymbol{d}_{0j}\right|^2}{\hbar\omega_{0j}}$

  Transition dipole moment
  $\boldsymbol{d}_{0j} = e\,\langle 0| \hat{\boldsymbol{r}} |j\rangle$



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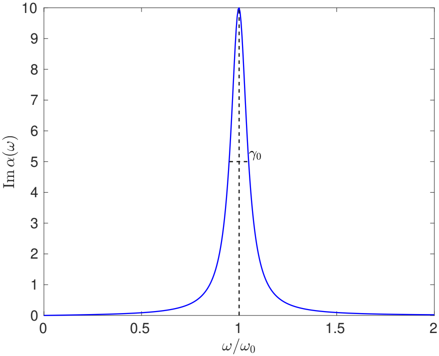
  $\boldsymbol{d}_{0j} = e\,\langle 0|\,\hat{\boldsymbol{r}}\,|j\rangle$
- Linewidth
  $\gamma_{0j} = \frac{\omega_{0j}^3\left|\boldsymbol{d}_{0j}\right|^2}{3\hbar\pi\varepsilon_0 c^3}$
  Natural broadening due to the interactions with the quantum vacuum



Oscillator strength

- Oscillator strength

$$f_{12} = \frac{2}{3}\frac{m_e}{\hbar^2}\left(E_2 - E_1\right)\left|\langle 1|\,\hat{\boldsymbol{r}}\,|2\rangle\right|^2$$

- Amplitude of polarisability

$$c_{0j} = \frac{2\left|\boldsymbol{d}_{0j}\right|^2}{\hbar\omega_{0j}}$$

Causality

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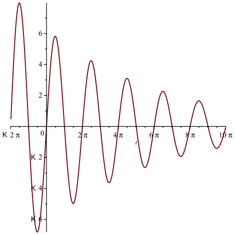

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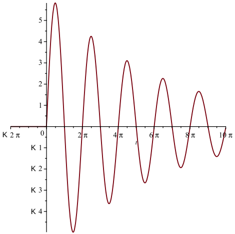

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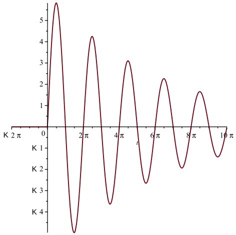

$$\alpha(\omega) = \frac{1}{i\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\alpha(\omega')}{\omega - \omega'}\mathrm{d}\omega'$$

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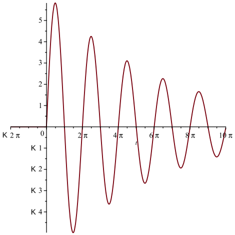
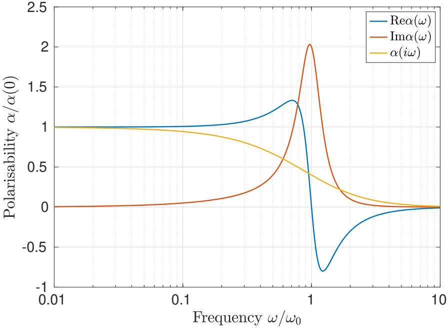


$$\alpha(\omega) = \frac{1}{i\pi}\mathcal{P}\int\limits_{-\infty}^{\infty}\frac{\alpha(\omega')}{\omega-\omega'}\mathrm{d}\omega'$$

- Separation into real and imaginary parts (using even and odd functions) $\rightarrow$ Kramers–Kronig relation

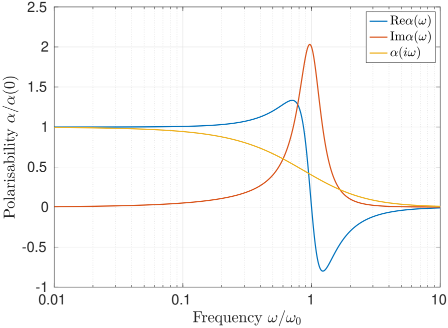
$$\mathrm{Re}\alpha(\omega) = \frac{2}{\pi}\mathcal{P}\int\limits_{0}^{\infty}\frac{\omega'\mathrm{Im}\alpha(\omega)}{\omega'^2-\omega^2}\mathrm{d}\omega'\,,\;\mathrm{Im}\alpha(\omega) = -\frac{2}{\pi}\int\limits_{0}^{\infty}\frac{\mathrm{Re}\alpha(\omega')}{\omega'^2-\omega^2}\mathrm{d}\omega'$$

Response functions with imaginary frequencies



Response functions with imaginary frequencies

- $\alpha(i\xi) = \frac{2}{\pi}\int\limits_0^\infty \frac{\omega \mathrm{Im}\alpha(\omega)}{\omega^2+\xi^2}\mathrm{d}\omega$



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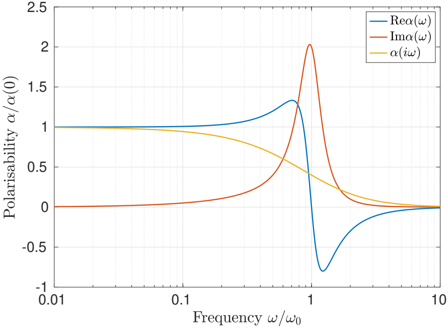
  monotonically decreasing



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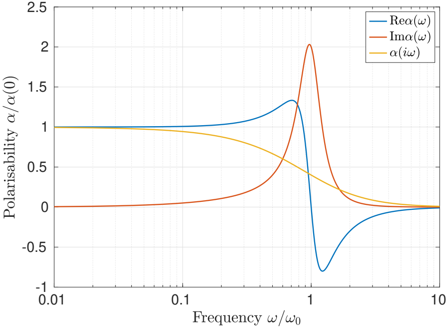

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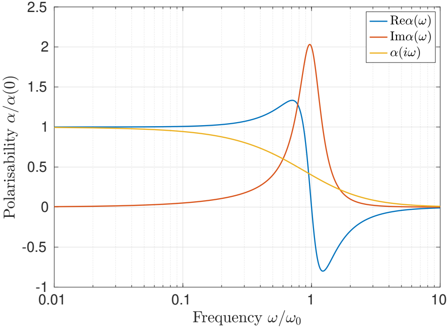
- $\mathrm{Im}\alpha(\omega \mapsto 0) \mapsto 0$
- $\mathrm{Re}\alpha(\omega), \mathrm{Im}\alpha(\omega), \alpha(\mathrm{i}\omega) \mapsto 0$
  for $\omega \mapsto \infty$



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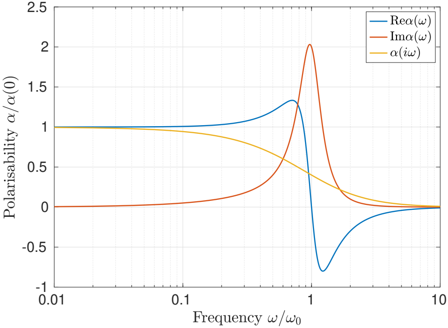
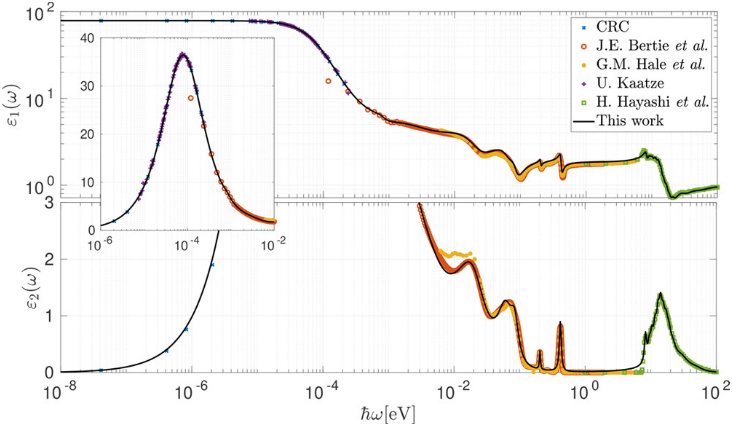


KKR restricts response functions to the class of causal functions

Dielectric function of water



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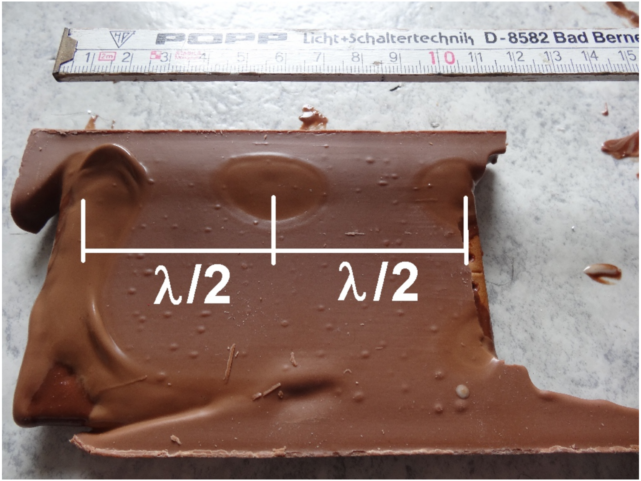

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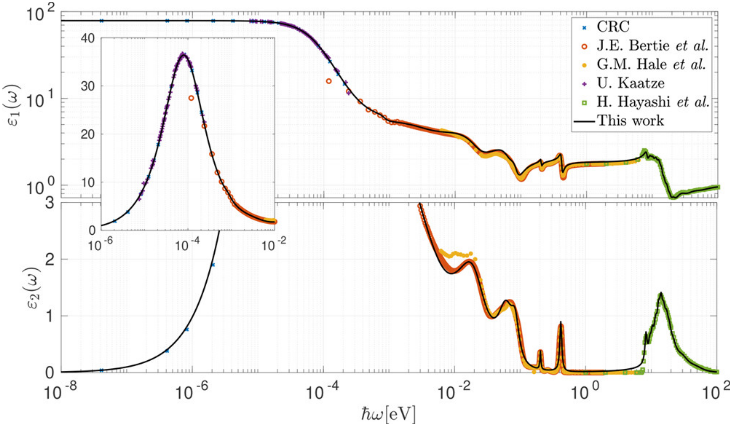

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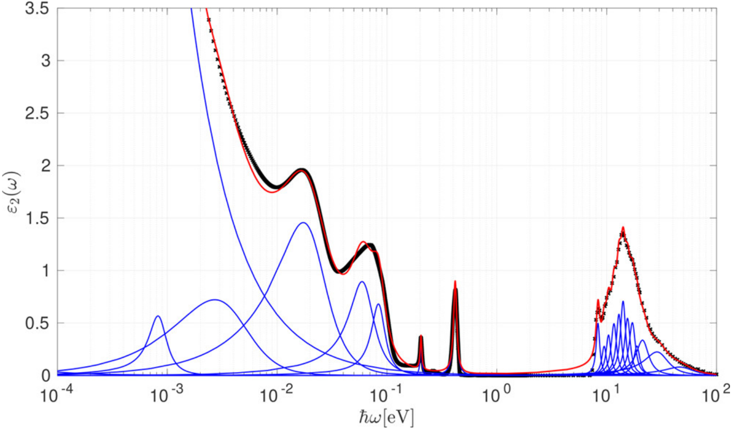

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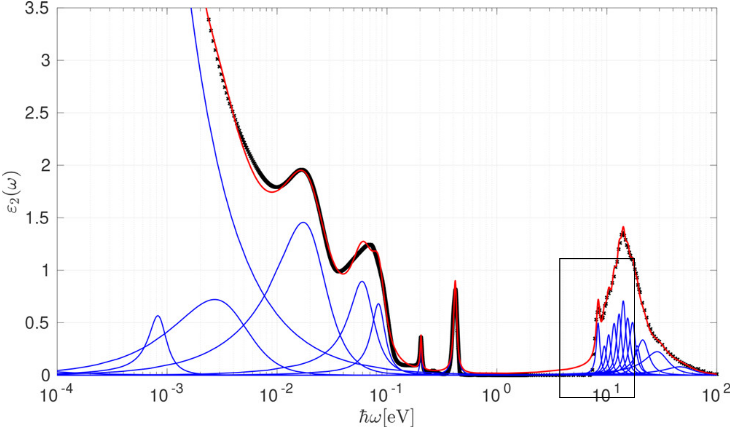

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Alternative way

$$\epsilon_1(\omega) = 1 + \sum_{k=1}^{N_{osc}} \frac{A_k(1-\omega^2 C_k + \omega H_2(\omega) B_k)}{[1-\omega^2 C_k + \omega H_2(\omega)B_k]^2 + [\omega H_1(\omega) B_k]^2},$$
$$\epsilon_2(\omega) = \sum_{k=1}^{N_{osc}} \frac{A_k \omega H_1(\omega) B_k}{[1-\omega^2 C_k + \omega H_2(\omega)B_k]^2 + [\omega H_1(\omega) B_k]^2}, \tag{10}$$

where we have replaced B_k with $B_k(\omega) = B_k H(\omega)$. The dielectric function at complex frequency then becomes

$$\epsilon(i\omega) = 1 + \sum_{k=1}^{N_{osc}} \frac{A_k}{1 + B_k \omega H_1(i\omega) + B_k \omega i H_2(i\omega) + C_k \omega^2}. \tag{11}$$

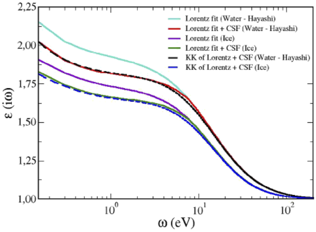
With the properties we have discussed so far, we see that, if $\omega > \omega_0$, $H_2(\omega)$ vanishes and both $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ recover the usual form of the Lorentz oscillator provided $H_1(\omega) \to 1$. On the other hand, if $\omega < \omega_0$, $\epsilon_2(\omega)$ vanishes altogether, as required. Additionally, for $\epsilon(i\omega)$ to remain continuous at $\omega = \omega_0$, we require $\lim_{\omega\to\omega_0}^{(-)}[\omega i H_2(i\omega)] = \omega_0$, which is most easily imposed by assuming $\omega i H_2(i\omega) = \omega_0$ for $\omega < \omega_0$.

With regard to the functions $H_1(\omega)$ and $H_2(\omega)$, we need them to remain real for imaginary frequencies. Furthermore, we require $H_1(\omega)$ to be symmetrical with respect to the transformation $\omega \to -\omega$, and conversely, we need $H_2(\omega)$ to be an odd function so that the whole satisfies $H(-\omega) = \overline{H}(\omega)$. These set of conditions may be satisfied by the choice,

$$H_1(\omega) = \frac{1}{2}\left(\tanh\frac{\omega^4 - \omega_0^4}{\Delta\omega} + \tanh\frac{\omega^4 + \omega_0^4}{\Delta\omega}\right), \tag{12}$$

$$H_2(\omega) = \frac{\omega_0}{2\omega}\left(\tanh\frac{\omega_0^4 - \omega^4}{\Delta\omega} + \tanh\frac{\omega^4 + \omega_0^4}{\Delta\omega}\right), \tag{13}$$

Kramers–Kronig one cannot avoid the use of special functions with no simple analytical form for $\epsilon(i\omega)$.[82] In practice, the deviations from Kramer–Kronig are very small. Figure 2 (top) compares $\epsilon(i\omega)$ obtained in analytical form from Eq. (11), with the Kramers–Kronig transformation of the parametric representation of $\kappa(\omega)$ computed through its relation with $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$. The two curves are clearly very similar on the scale of the figure and differ at most by 3%. In the same figure, we also show the results obtained from the plain Lorentz model. The curves are almost identical for energies above the first electronic excitation but differ significantly for lower energies. Thanks to the truncation of the Lorentz oscillators, the



[0] J. Luengo-Márquez, F. Izquierdo-Ruiz, and L. G. MacDowell: *Intermolecular forces at ice and water interfaces: Premelting, surface freezing, and regelation*, J. Chem. Phys. **157**, 044704 (2022).

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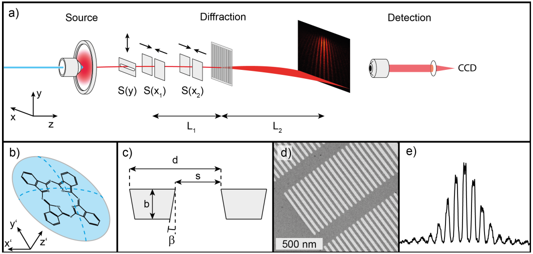
Matter-wave interferometry with large molecules



C. Brand, JF *et al.*, Ann. Phys. (Berlin) **527**, 580 (2015)

Typical parameters:

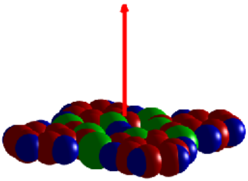
Distances: $L_1 \approx L_2 \approx 0.8\mathrm{m}$

Grating: SiN_x, Period $100\mathrm{nm}$, Thickness $10-100\mathrm{nm}$

Molecule: Phthalocyanine, $m = 514\mathrm{u}$, $v = 180-250\frac{\mathrm{m}}{\mathrm{s}}$, $\lambda \approx 1\mathrm{pm}$

Realisation in group of Prof. M. Arndt, U. Vienna.

Polarisability density



- Interaction: Dipole acting on centre-of-mass

[1] D.F. Parsons, B.W. Ninham. J. Phys. Chem. A **113**, 1141 (2009).

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- Interaction: Dipole acting on centre-of-mass
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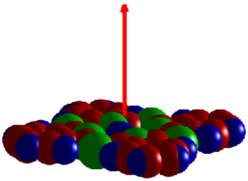

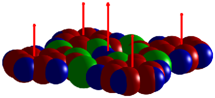

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Polarisability density

- Interaction: Dipole acting on centre-of-mass
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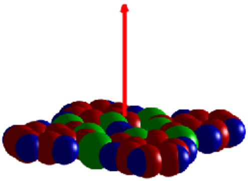
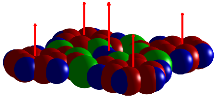
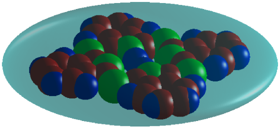
- Transition to continuous density

$$\eta(\boldsymbol{r}) = \frac{1}{\mathcal{N}} \exp\left\{-\left(\frac{x^2}{a_x^2} + \frac{y^2}{a_y^2} + \frac{z^2}{a_z^2}\right)\right\}$$







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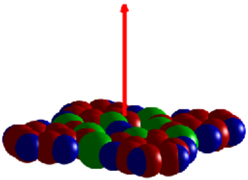
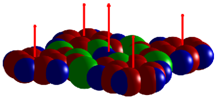
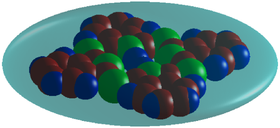
- Gaussian distribution with main axis a_x, a_y and a_z, determined by:







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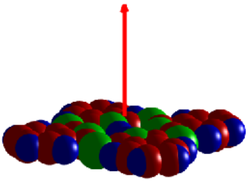

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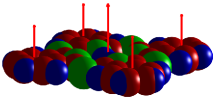
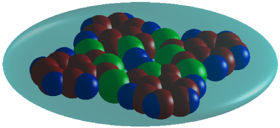


- Gaussian distribution with main axis a_x, a_y and a_z, determined by:
  - Volume of electron density[1]



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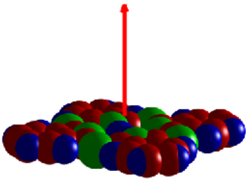
Polarisability density



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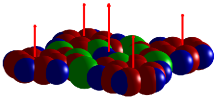

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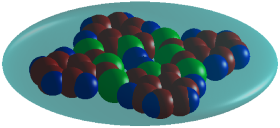

- Gaussian distribution with main axis a_x, a_y and a_z, determined by:
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  - Main axis due to static value $\alpha_{ii}(0) = g a_i$

[1] D.F. Parsons, B.W. Ninham. J. Phys. Chem. A **113**, 1141 (2009).

Averaging the potential

- spatial density + dynamical polarisability $\boldsymbol{\alpha}(\boldsymbol{r},\omega) = \eta(\boldsymbol{r})\boldsymbol{\alpha}(\omega)$

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- Potential at each point of the molecule

$$\tilde{U}_{CP}(\mathbf{r}_A+\boldsymbol{R}^{-1}\cdot\boldsymbol{\varrho})=\frac{\hbar\mu_0}{4\pi}\int_0^\infty d\xi\,\xi^2\eta(\boldsymbol{\varrho})\,\mathrm{Tr}\left[\boldsymbol{R}^{-1}\cdot\boldsymbol{\alpha}(i\xi)\cdot\boldsymbol{R}\right.$$
$$\left.\cdot\boldsymbol{G}(\mathbf{r}_A+\boldsymbol{R}^{-1}\cdot\boldsymbol{\varrho},\mathbf{r}_A+\boldsymbol{R}^{-1}\cdot\boldsymbol{\varrho},i\xi)\right]$$

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- Rotation matrix **R**
- Casimir–Polder Potential

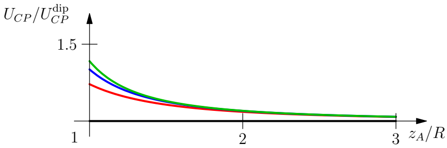
$$U_{CP}(\mathbf{r}_A) = \int \mathrm{d}\Omega \int_V d^3\varrho\,\tilde{U}_{CP}(\mathbf{r}_A + \boldsymbol{R}^{-1}(\Omega)\cdot\boldsymbol{\varrho})$$

Results of the finite-size effects

$$U_{CP}(z_A) = U_{CP}^{dip}(z_A) \sum_{n=0}^{\infty} c_n \left(\frac{a}{z_A}\right)^n$$

$$\approx U_{CP}^{dip}(z_A) \left[1 + \frac{1}{2}\left(\frac{a}{z_A}\right)^2 + \frac{3}{4}\left(\frac{a}{z_A}\right)^4\right]$$

- Corrections in terms of a/z_A (ratio between extension and distance)
- Analogy to higher-order (quadrupole, octopole, ...)



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Summary of last lecture

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- Field quantisation: field excitation addresses photons and media excitations

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

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- Van-der-Waals potential

$$U_{vdW}(\boldsymbol{r}_A,\boldsymbol{r}_B) = -\frac{\hbar\mu_0^2}{2\pi}\int_0^\infty \mathrm{d}\xi\,\xi^4\,\mathrm{tr}\left[\boldsymbol{\alpha}_A(i\xi)\cdot\mathbf{G}(\boldsymbol{r}_A,\boldsymbol{r}_B,i\xi)\cdot\boldsymbol{\alpha}_B(i\xi)\cdot\mathbf{G}(\boldsymbol{r}_B,\boldsymbol{r}_A,i\xi)\right]$$

Summary of last lecture

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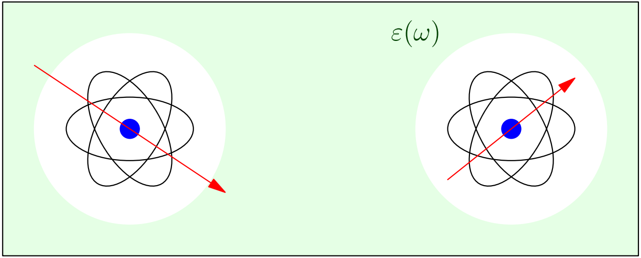
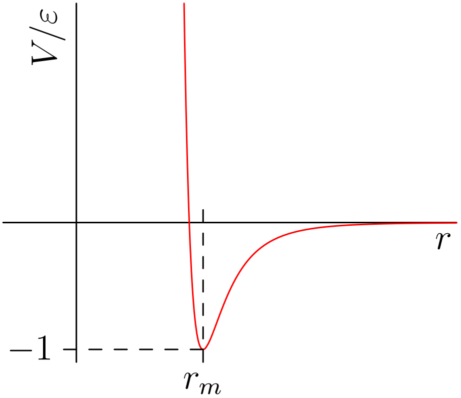
- Interpretation as virtual photon exchange (propagating virtual photons)

Medium-assisted dispersion forces



Pauli blocking



- Small distances (solvent - molecule); Lennard–Jones potential

$$V(r) = \varepsilon \left(\frac{r_m}{r}\right)^6 \left[\left(\frac{r_m}{r}\right)^6 - 2\right]$$

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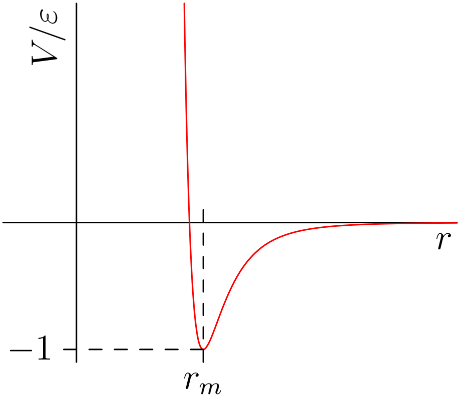

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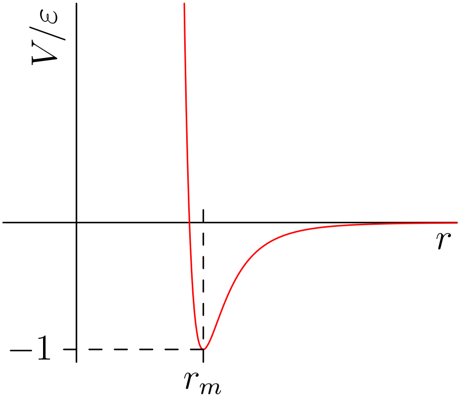
Pauli blocking



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- Particle embedded in a cavity

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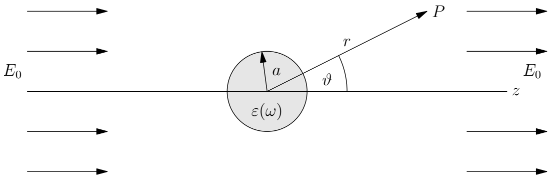
Dielectric sphere in e field



- Dielectric sphere $\varepsilon(\omega)$ and radius a
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[0] J.D. JACKSON. *classical electrodynamics*, 3th edition, Walter de Gruyter (2002).

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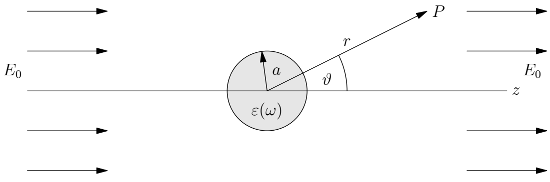

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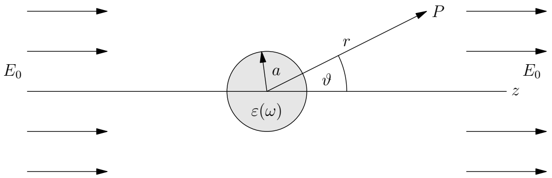

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  - inside: $\Phi_i = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\vartheta)$

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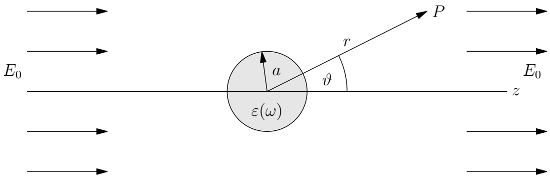

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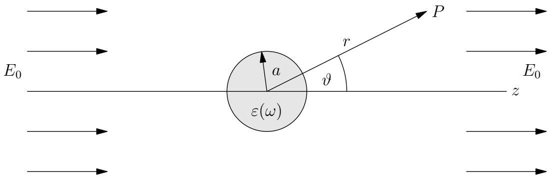

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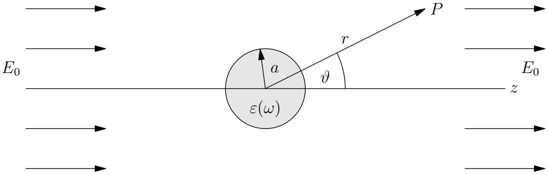

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[0] J.D. Jackson. *classical electrodynamics*, 3th edition, Walter de Gruyter (2002).

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Dielectric sphere in e field

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- Second: $\varepsilon(\omega)A_1 = -E_0 - 2C_1/a^3$ and $\varepsilon(\omega)lA_1 = -(l+1)C_l/a^{2l+1}$ for $l > 1$

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- Second: $\varepsilon(\omega)A_1 = -E_0 - 2C_1/a^3$ and $\varepsilon(\omega)lA_1 = -(l+1)C_l/a^{2l+1}$ for $l > 1$
- Green: accomplished when $A_l = C_l = 0$
- Red: acc. when $A_1 = -\frac{3}{2+\varepsilon(\omega)}E_0$ & $C_1 = \frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2}a^3 E_0$

Dielectric sphere in e field

- potential inside: $\Phi_i = -\frac{3}{2+\varepsilon(\omega)} E_0 r \cos\vartheta$
- potential outside: $\Phi_o = -E_0 r \cos\vartheta + \frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} a^3 E_0 \frac{1}{r^2} \cos\vartheta$

Dielectric sphere in e field

- potential inside: $\Phi_i = -\frac{3}{2+\varepsilon(\omega)} E_0 r \cos\vartheta \rightarrow E_i = \frac{3}{\varepsilon(\omega)+2} E_0$
- potential outside: $\Phi_o = -E_0 r \cos\vartheta + \frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} a^3 E_0 \frac{1}{r^2} \cos\vartheta$

- potential of dipole: $\varphi = \frac{1}{4\pi\varepsilon_0} \frac{d\cos\vartheta}{r^2} \rightarrow d = 4\pi\varepsilon_0 \frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} a^3 E_0$

Dielectric sphere in e field

- potential inside: $\Phi_i = -\frac{3}{2+\varepsilon(\omega)} E_0 r \cos\vartheta \to E_i = \frac{3}{\varepsilon(\omega)+2} E_0$
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  $$E_o = E_0 + E_d$$
- potential of dipole: $\varphi = \frac{1}{4\pi\varepsilon_0} \frac{d\cos\vartheta}{r^2} \to d = 4\pi\varepsilon_0 \frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} a^3 E_0$
- Comparison with induced dipole: $d = \alpha E$:

Dielectric sphere in e field

- potential inside: $\Phi_i = -\frac{3}{2+\varepsilon(\omega)} E_0 r \cos\vartheta \rightarrow E_i = \frac{3}{\varepsilon(\omega)+2} E_0$
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  $$E_o = E_0 + E_d$$
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- Comparison with induced dipole: $d = \alpha E$: $\alpha = 4\pi\varepsilon_0 \frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} a^3$

Dielectric sphere in e field

- potential inside: $\Phi_i = -\frac{3}{2+\varepsilon(\omega)} E_0 r \cos\vartheta \to E_i = \frac{3}{\varepsilon(\omega)+2} E_0$
- potential outside: $\Phi_o = -E_0 r \cos\vartheta + \frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} a^3 E_0 \frac{1}{r^2} \cos\vartheta$
  $$E_o = E_0 + E_d$$
- potential of dipole: $\varphi = \frac{1}{4\pi\varepsilon_0} \frac{d\cos\vartheta}{r^2} \to d = 4\pi\varepsilon_0 \frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} a^3 E_0$
- Comparison with induced dipole: $d = \alpha E$: $\alpha = 4\pi\varepsilon_0 \frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} a^3$
- Clausius–Mossotti relation: Connection between intensive and extensive dielectric quantities

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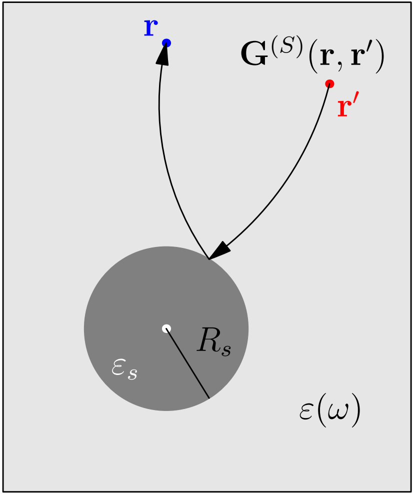
Hard-sphere model

- Clausius–Mossotti relation

$$\alpha = 4\pi\varepsilon_0 \frac{\varepsilon_S(\omega) - 1}{\varepsilon_S(\omega) + 2} R_s^3$$

Hard-sphere model

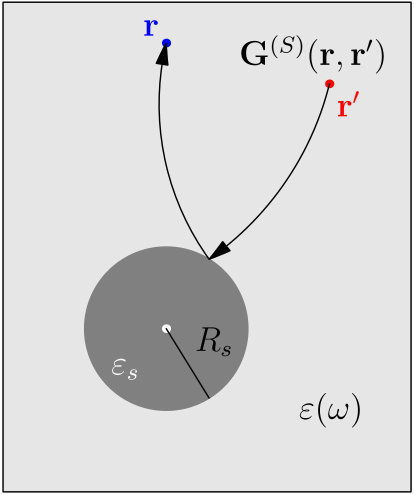


- Clausius–Mossotti relation

$$\alpha = 4\pi\varepsilon_0 \frac{\varepsilon_S(\omega)-1}{\varepsilon_S(\omega)+2} R_s^3$$

- Add environmental medium $\varepsilon(\omega)$

Hard-sphere model



- Clausius–Mossotti relation

$$\alpha = 4\pi\varepsilon_0 \frac{\varepsilon_S(\omega)-1}{\varepsilon_S(\omega)+2} R_s^3$$

- Add environmental medium $\varepsilon(\omega)$
- Same calculation yields Hard-sphere model

$$\alpha_{HS} = 4\pi\varepsilon_0\varepsilon(\omega) \frac{\varepsilon_S(\omega)-\varepsilon(\omega)}{\varepsilon_S(\omega)+2\varepsilon(\omega)} R_s^3$$

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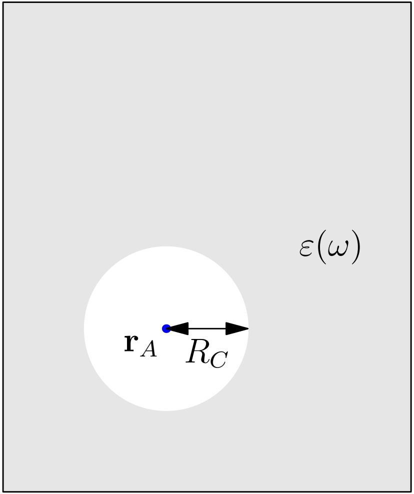
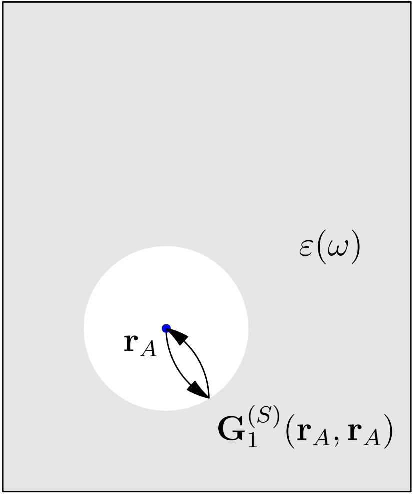
Real cavity model



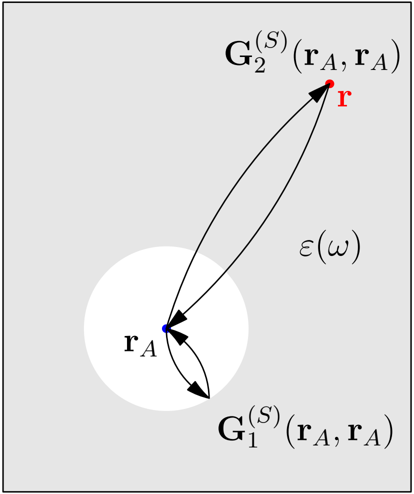
- vacuum bubble R_C embedded in medium $\varepsilon(\omega)$

Real cavity model



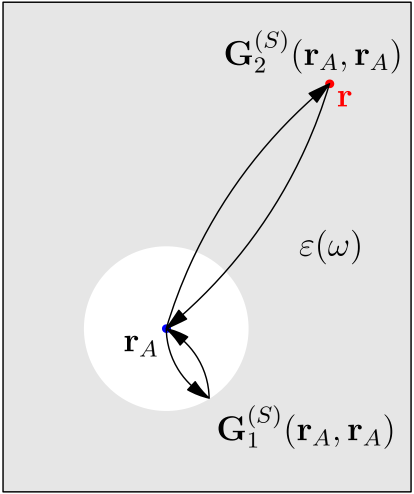
- vacuum bubble R_C embedded in medium $\varepsilon(\omega)$
- scattering process:
  - reflection at the cavity's boundary

Real cavity model



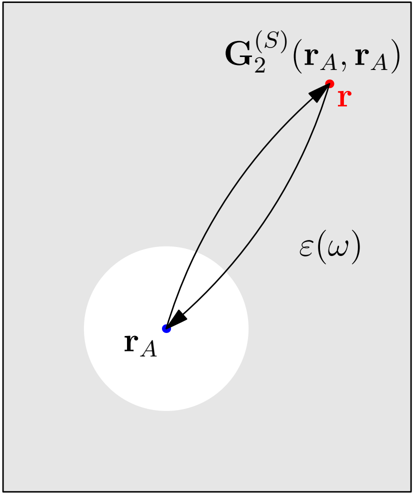
- vacuum bubble R_C embedded in medium $\varepsilon(\omega)$
- scattering process:
  - reflection at the cavity's boundary
  - transmission through the boundary to point ***r*** + back-reflection

Real cavity model

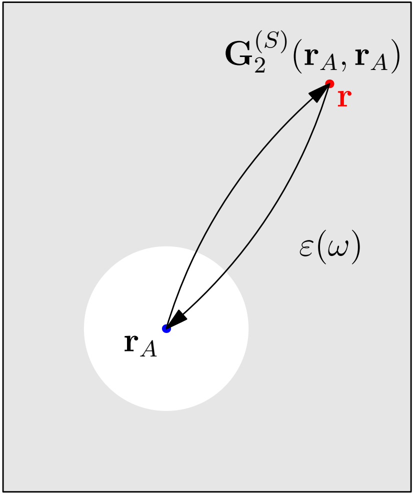


- vacuum bubble R_C embedded in medium $\varepsilon(\omega)$
- scattering process:
  - reflection at the cavity's boundary
  - transmission through the boundary to point $\boldsymbol{r}$ + back-reflection
  - Negligence of multiple scattering

Real cavity model



Real cavity model



- transmission through boundary

$$\mathbf{G}(\boldsymbol{r}, \boldsymbol{r}_A, \omega) = \frac{\mu(\omega) q}{4\pi} D(\omega) \times \left[a(q)\mathbf{I} - b(q)\mathbf{v} \otimes \mathbf{v}\right] \mathrm{e}^{iq}$$

with

- $a(q) = 1/q + i/q^2 - 1/q^3$
- $b(q) = 1/q + 3i/q^2 - 3/q^3$
- $q = |\boldsymbol{r} - \boldsymbol{r}_A| \sqrt{\varepsilon(\omega)\mu(\omega)}\omega/c$
- $\mathbf{v} = (\boldsymbol{r} - \boldsymbol{r}_A) / |\boldsymbol{r} - \boldsymbol{r}_A|$

Real cavity model

- arrival and departure (Born series expansion)

$$\mathbf{G}_2^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A, \omega) = (\varepsilon(\omega) - 1)\frac{\omega^2}{c^2}\mathbf{G}(\boldsymbol{r}_A, \boldsymbol{r}, \omega)\mathbf{G}(\boldsymbol{r}, \boldsymbol{r}_A, \omega)$$

Real cavity model

- arrival and departure (Born series expansion)

$$\mathbf{G}_2^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A, \omega) = (\varepsilon(\omega) - 1)\frac{\omega^2}{c^2}\mathbf{G}(\boldsymbol{r}_A, \boldsymbol{r}, \omega)\mathbf{G}(\boldsymbol{r}, \boldsymbol{r}_A, \omega)$$

- Comparison with propagation in bulk medium

$$\mathbf{G}_2^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A\omega) = D^2(\omega)\mathbf{G}_{bulk}^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A, \omega)$$

Real cavity model

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$$\mathbf{G}_2^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A, \omega) = (\varepsilon(\omega) - 1)\frac{\omega^2}{c^2}\mathbf{G}(\boldsymbol{r}_A, \boldsymbol{r}, \omega)\mathbf{G}(\boldsymbol{r}, \boldsymbol{r}_A, \omega)$$

- Comparison with propagation in bulk medium

$$\mathbf{G}_2^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A\omega) = D^2(\omega)\mathbf{G}_{bulk}^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A, \omega)$$

- With the transmission coefficient

$$D(\omega) = \frac{j_1(z_0)\left[z_0 h_1^{(1)}(z_0)\right]' - [z_0 j_1(z_0)]' \, h_1^{(1)}(z_0)}{\mu(\omega)\left[j_1(z_0)\left[z h_1^{(1)}(z)\right]' - \varepsilon(\omega)\,[z_0 j_1(z_0)]' \, h_1^{(1)}(z)\right]}$$

Real cavity model

- transmission coefficient

$$D(\omega) = \frac{j_1(z_0)\left[z_0 h_1^{(1)}(z_0)\right]' - [z_0 j_1(z_0)]'\, h_1^{(1)}(z_0)}{\mu(\omega)\left[j_1(z_0)\left[z h_1^{(1)}(z)\right]' - \varepsilon(\omega)\,[z_0 j_1(z_0)]'\, h_1^{(1)}(z)\right]}$$

Real cavity model

- transmission coefficient

$$D(\omega) = \frac{j_1(z_0)\left[z_0 h_1^{(1)}(z_0)\right]' - [z_0 j_1(z_0)]' h_1^{(1)}(z_0)}{\mu(\omega)\left[j_1(z_0)\left[z h_1^{(1)}(z)\right]' - \varepsilon(\omega)[z_0 j_1(z_0)]' h_1^{(1)}(z)\right]}$$

- Taylor series expansion ($\omega R_c/c \ll 1$)

$$D(\omega) \approx \frac{3\varepsilon(\omega)}{1+2\varepsilon(\omega)} - \frac{3}{10}\frac{\varepsilon(\omega)\left[10\varepsilon^2(\omega)\mu(\omega) - 5\varepsilon(\omega)\mu(\omega) - 4\varepsilon(\omega) - 1\right)}{[1+2\varepsilon(\omega)]^2}\left(\frac{\omega R_C}{c}\right)^2$$

Real cavity model

- transmission coefficient for small cavity ($R_C \to 0$)

$$D(\omega) = \frac{3\varepsilon(\omega)}{1 + 2\varepsilon(\omega)}$$

Real cavity model

- transmission coefficient for small cavity ($R_C \to 0$)

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$$\mathbf{G}_2^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A\omega) = D^2(\omega)\mathbf{G}_{bulk}^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A, \omega)$$

Real cavity model

- transmission coefficient for small cavity ($R_C \to 0$)

$$D(\omega) = \frac{3\varepsilon(\omega)}{1 + 2\varepsilon(\omega)}$$

- scattering Green tensor

$$\mathbf{G}_2^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A\omega) = D^2(\omega)\mathbf{G}_{bulk}^{(S)}(\boldsymbol{r}_A, \boldsymbol{r}_A, \omega)$$

- vdW potential

$$U_{vdW}(\boldsymbol{r}_A, \boldsymbol{r}_B) \propto \left(\frac{3\varepsilon(i\xi)}{2\varepsilon(i\xi) + 1}\right)^4 \alpha_A(i\xi)\alpha_B(i\xi)\,\mathrm{tr}\,\mathbf{G}(\boldsymbol{r}_A, \boldsymbol{r}_B, i\xi)\mathbf{G}(\boldsymbol{r}_B, \boldsymbol{r}_A, i\xi)$$

Real cavity model

- transmission coefficient for small cavity ($R_C \to 0$)

$$D(\omega) = \frac{3\varepsilon(\omega)}{1 + 2\varepsilon(\omega)}$$

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$$U_{vdW}(\boldsymbol{r}_A, \boldsymbol{r}_B) \propto \left(\frac{3\varepsilon(i\xi)}{2\varepsilon(i\xi)+1}\right)^4 \alpha_A(i\xi)\alpha_B(i\xi)\,\mathrm{tr}\,\mathbf{G}(\boldsymbol{r}_A, \boldsymbol{r}_B, i\xi)\mathbf{G}(\boldsymbol{r}_B, \boldsymbol{r}_A, i\xi)$$

$$\alpha_{Ons}(i\xi) = \left(\frac{3\varepsilon(i\xi)}{2\varepsilon(i\xi)+1}\right)^2 \alpha(i\xi)$$

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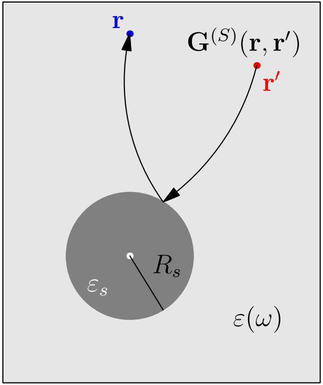
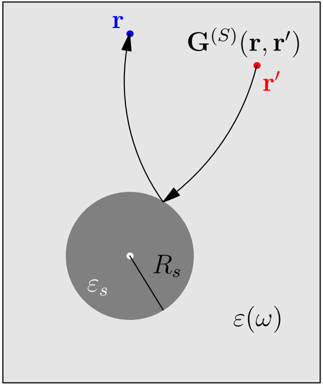
Scattering at a dielectric sphere

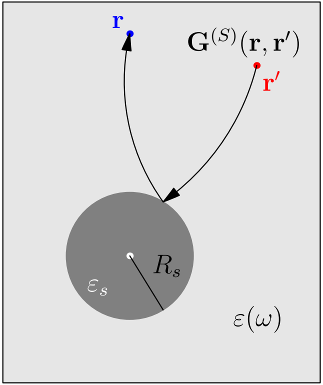


Scattering at a dielectric sphere

- Dielectric sphere ε_s, radius R_s embedded in medium $\varepsilon(\omega)$

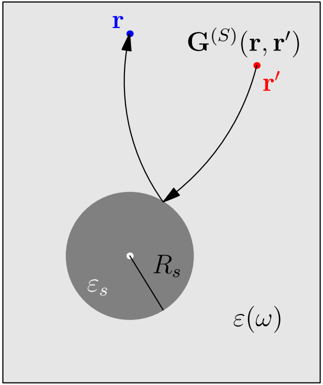


Scattering at a dielectric sphere



- Dielectric sphere ε_s, radius R_s embedded in medium $\varepsilon(\omega)$
- Reflection outside

Scattering at a dielectric sphere



- Dielectric sphere ε_s, radius R_s embedded in medium $\varepsilon(\omega)$
- Reflection outside
- Green function with $k = \sqrt{\varepsilon(\omega)\mu(\omega)}\omega/c$

$$\mathbf{G}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu k}{4\pi} \times \sum_{p=\pm}\sum_{l=0}^{\infty}\sum_{m=0}^{l}[2-\delta_{m0}]\frac{2l+1}{l(l+1)} \times \frac{(l-m)!}{l+m)!}\Big[B_l^M \mathbf{M}_{lm}^p(k,\boldsymbol{r})\otimes\mathbf{M}_{lm}^p(k,\boldsymbol{r}') + B_l^N \mathbf{N}_{lm}^p(k,\boldsymbol{r})\otimes\mathbf{N}_{lm}^p(k,\boldsymbol{r}')\Big]$$

Scattering at a dielectric sphere

- Reflection coefficients

$$B_l^M = -\frac{\mu k_s j_l(z)\,[z_s j_l(z_s)]' - \mu_s k j_l(z_s)\,[z j_l(z)]'}{\mu k_s h_l^{(1)}(z)\,[z_s j_l(z_s)]' - \mu_s k j_l(z_s\left[z h_l^{(1)}(z)\right]'}$$

$$B_l^N = -\frac{\mu k_s j_l(z_s)\,[z j_l(z)]' - \mu_s k j_l(z)\,[z_s j_l(z_s)]'}{\mu k_s j_l(z_s)\left[z h_l^{(1)}(z)\right]' - \mu_s k h_l^{(1)}(z)\,[z_s j_l(z_s)]'}$$

with $z = kR_s$, $z_s = k_s R_s$ and $k_s = \sqrt{\varepsilon_s \mu_s}\omega/c$

Scattering at a dielectric sphere

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with $z = kR_s$, $z_s = k_s R_s$ and $k_s = \sqrt{\varepsilon_s \mu_s}\,\omega/c$

- small sphere limit $R \ll c/\omega$: only $l = 1$ contributes

$$B_1^M = \frac{2i}{3}\left(\sqrt{\varepsilon\mu}\frac{\omega R}{c}\right)^3 \frac{\mu_s - \mu}{\mu_s + 2\mu}\,, \quad B_1^N = \frac{2i}{3}\left(\sqrt{\varepsilon\mu}\frac{\omega R}{c}\right)^3 \frac{\varepsilon_s - \varepsilon}{\varepsilon_s + 2\varepsilon}$$

Scattering at a dielectric sphere

- Taking coincidence limit $\boldsymbol{r}' \to \boldsymbol{r}$

Scattering at a dielectric sphere

- Taking coincidence limit $\boldsymbol{r}' \to \boldsymbol{r}$
- Comparison with Green tensor by propagating through bulk medium $\mathbf{G}^{(0)}(\boldsymbol{r}, \mathbf{0}, \omega)$

$$\mathbf{G}(\boldsymbol{r}, \boldsymbol{r}, \omega) = 4\pi\varepsilon_0\varepsilon R^3 \frac{\varepsilon_s - \varepsilon}{\varepsilon_s + 2\varepsilon} \frac{\omega^2}{c^2} \mathbf{G}^{(0)}(\boldsymbol{r}, \mathbf{0}, \omega) \cdot \mathbf{G}^{(0)}(\mathbf{0}, \boldsymbol{r}, \omega)$$
$$- \frac{4\pi R^3}{\mu} \frac{\mu_s - \mu}{\mu_s + 2\mu} \mathbf{G}^{(0)}(\boldsymbol{r}, \mathbf{r}_s, \omega) \times \nabla_s \cdot \nabla_s \times \mathbf{G}^{(0)}(\mathbf{r}_s, \boldsymbol{r}, \omega)\Big|_{\mathbf{r}_s = \mathbf{0}}$$

Scattering at a dielectric sphere

- Taking coincidence limit $\boldsymbol{r}' \to \boldsymbol{r}$
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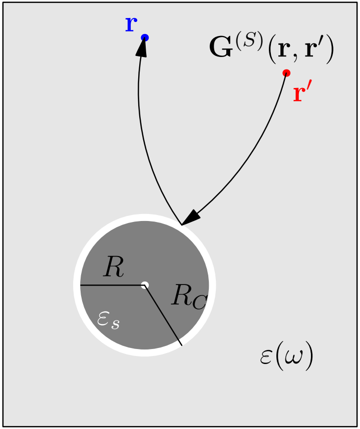
$$- \frac{4\pi R^3}{\mu} \frac{\mu_s - \mu}{\mu_s + 2\mu} \mathbf{G}^{(0)}(\boldsymbol{r}, \mathbf{r}_s, \omega) \times \nabla_s \cdot \nabla_s \times \mathbf{G}^{(0)}(\mathbf{r}_s, \boldsymbol{r}, \omega)\Big|_{\mathbf{r}_s = \mathbf{0}}$$

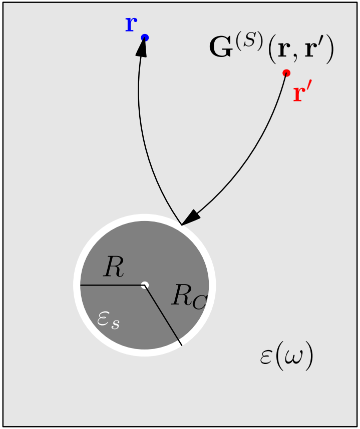
- excess polarisability and magnetizability

$$\alpha_s^\star = 4\pi\varepsilon_0\varepsilon R^3 \frac{\varepsilon_s - \varepsilon}{\varepsilon_s + 2\varepsilon}, \quad \beta_s^\star = \frac{4\pi R^3}{\mu_0} \frac{\mu_s - \mu}{\mu_s + 2\mu}$$

Sphere in a cavity

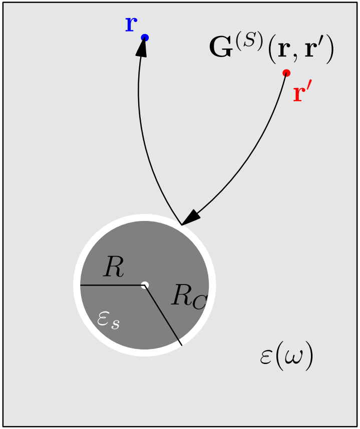


Sphere in a cavity



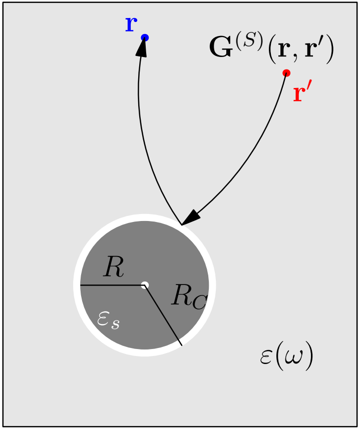
- Dielectric sphere ε_s, radius R embedded in medium $\varepsilon(\omega)$ with cavity $\varepsilon = 1$ and radius R_C

Sphere in a cavity



- Dielectric sphere ε_s, radius R embedded in medium $\varepsilon(\omega)$ with cavity $\varepsilon = 1$ and radius R_C
- Reflection outside

Sphere in a cavity



- Dielectric sphere ε_s, radius R embedded in medium $\varepsilon(\omega)$ with cavity $\varepsilon = 1$ and radius R_C
- Reflection outside
- Green function with $k = \sqrt{\varepsilon(\omega)\mu(\omega)}\omega/c$

$$\mathbf{G}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu k}{4\pi}\sum_{p=\pm}\sum_{l=0}^{\infty}\sum_{m=0}^{l}[2-\delta_{m0}]\,\frac{2\cdots}{l(\cdots}$$
$$\times\frac{(l-m)!}{(l+m)!}\Big[B_l^M\mathbf{M}_{lm}^p(k,\boldsymbol{r})\otimes\mathbf{M}_{lm}^p(k,\boldsymbol{r}')\cdots$$
$$+B_l^N\mathbf{N}_{lm}^p(k,\boldsymbol{r})\otimes\mathbf{N}_{lm}^p(k,\boldsymbol{r}')\Big]$$

Sphere in a cavity

- Reflection coefficients (three-layer system), for small R and R_C

$$B_1^M = \frac{2i}{3}\left(\sqrt{\varepsilon\mu}\frac{\omega}{c}\right)^3$$

$$\times\left[R_C^3\frac{1-\mu}{1+2\mu}+\frac{9\mu R^3(\mu_s-1)/(2\mu+1)}{\mu_s+2)(2\mu+1)+2(\mu_s-1)(1-\mu)R^3/R_C^3}\right]$$

$$B_1^N = \frac{2i}{3}\left(\sqrt{\varepsilon\mu}\frac{\omega}{c}\right)^3$$

$$\times\left[R_C^3\frac{1-\varepsilon}{1+2\varepsilon}+\frac{9\varepsilon R^3(\varepsilon_s-1)/(2\varepsilon+1)}{(\varepsilon_s+2)(2\varepsilon+1)+2(\varepsilon_s-1)(1-\varepsilon)R^3/R_C^3}\right]$$

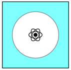
Sphere in a cavity

- Rewriting the reflection coefficients to polarisabilities

$$
\begin{aligned}
\alpha^\star_{S+C} &= \alpha^\star_C + \frac{\alpha_S}{\varepsilon}\left(\frac{3\varepsilon}{2\varepsilon+1}\right)^2 \frac{1}{1+\alpha^\star_C\alpha_S/(8\pi^2\varepsilon_0^2 R_C^6)} \\
\beta^\star_{S+C} &= \beta^\star_C + \beta_S\mu\left(\frac{3}{2\mu+1}\right)^2 \frac{1}{1+\beta^\star_C\beta_S\mu_0^2/(8\pi^2 R_C^6)}
\end{aligned}
$$

Excess Polarisabilities

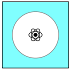
Onsager's real cavity



$$\alpha^{\star}_{Ons} = \alpha \left(\frac{3\varepsilon_1}{2\varepsilon_1 + 1} \right)^2$$

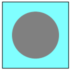
Excess Polarisabilities

Onsager's real cavity



$$\alpha^{\star}_{Ons} = \alpha\left(\frac{3\varepsilon_1}{2\varepsilon_1 + 1}\right)^2$$

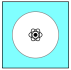
Hard-sphere model



$$\alpha^{\star}_{HS} = 4\pi\varepsilon_0\varepsilon_1 a^3\,\frac{\varepsilon - \varepsilon_1}{\varepsilon + 2\varepsilon_1}$$

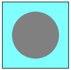
Excess Polarisabilities

Onsager's real cavity



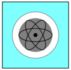
$$\alpha^\star_{Ons} = \alpha\left(\frac{3\varepsilon_1}{2\varepsilon_1+1}\right)^2$$

Hard-sphere model



$$\alpha^\star_{HS} = 4\pi\varepsilon_0\varepsilon_1 a^3\,\frac{\varepsilon-\varepsilon_1}{\varepsilon+2\varepsilon_1}$$

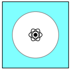
Finite-size particle



$$\alpha^\star_{fs} = \alpha^\star_C + \frac{\alpha^\star_{Ons}}{1+2\alpha^\star_C\alpha/(8\pi^2\varepsilon_0^2\varepsilon_1 a_2^6)}$$

Excess Polarisabilities

Onsager's real cavity



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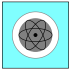

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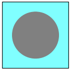

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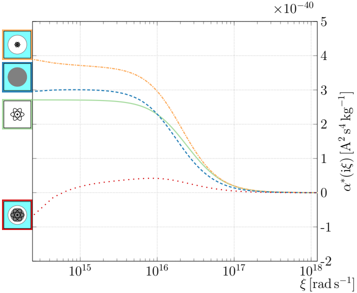

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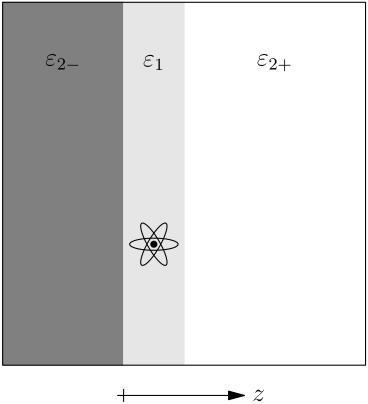
Casimir–Polder forces in layered media



- Polarisable particle in centred layer ε_1 of thickness L

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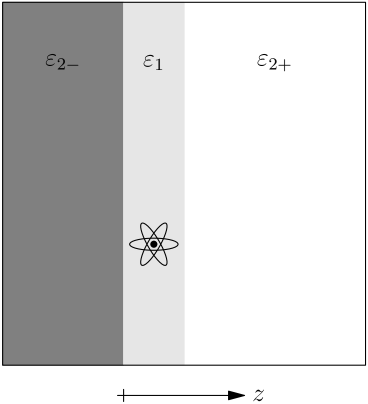

- Polarisable particle in centred layer ε_1 of thickness L
- Left and right enclosed by media $\varepsilon_{2\mp}$

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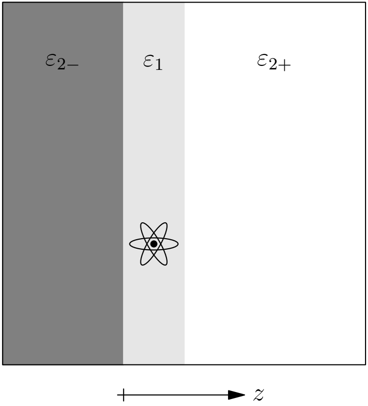

- Polarisable particle in centred layer ε_1 of thickness L
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- Three-layer system (well-known in literature)

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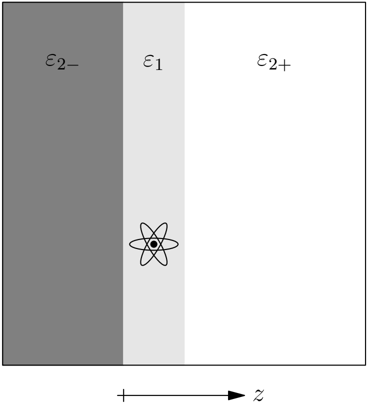

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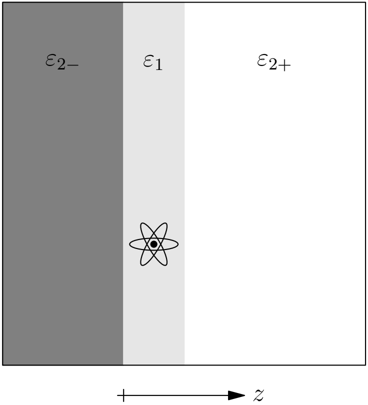

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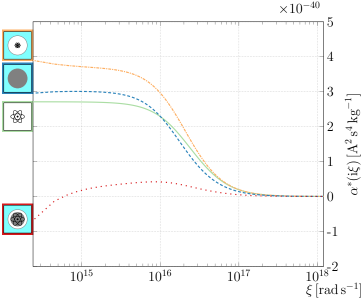

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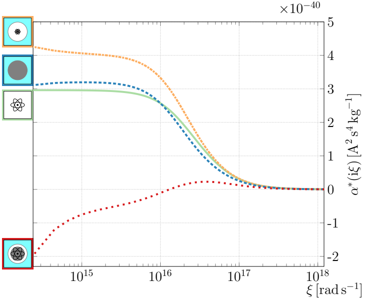

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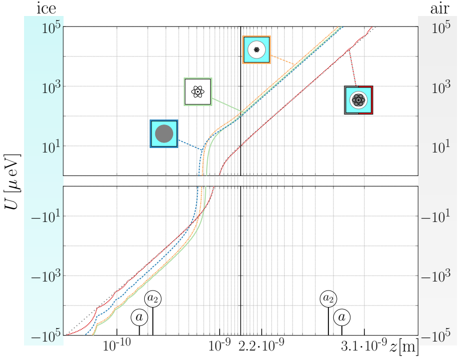
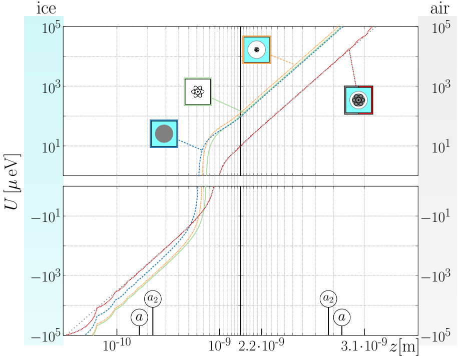
Casimir–Polder forces in layered media



- Methane: similar behaviour, different orders of magnitude

[1] JF, D.F. Parsons *et al.*, *Impact of effective polarisability models on the near-field interaction of dissolved greenhouse gases at ice and air interfaces*, Phys. Chem. Chem. Phys. **21**, 21296 (2019).

Casimir–Polder forces in layered media



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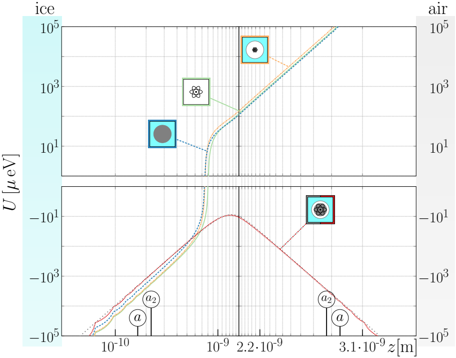

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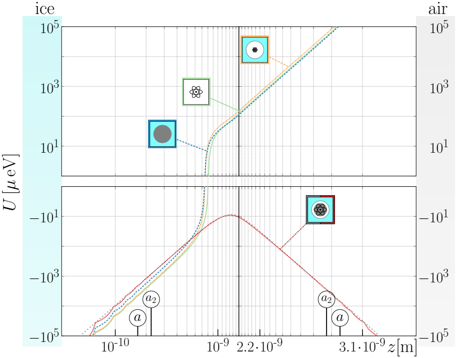

- Methane: similar behaviour, different orders of magnitude
- Attractive to water-ice interface repulsive from water-air interface
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- Methane will be captured; Carbon dioxide released[1]

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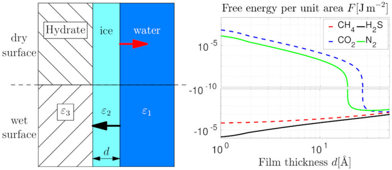
Stabilisation of gas hydrates



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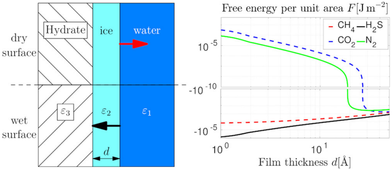
Stabilisation of gas hydrates

- Hydyrates: ice + gas



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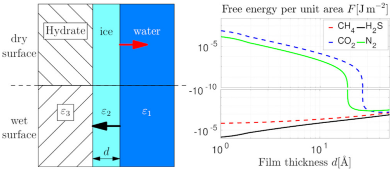
Stabilisation of gas hydrates

- Hydyrates: ice + gas
- Modelling via Lorentz–Lorenz $\varepsilon = \frac{1+2\Gamma}{1-\Gamma}$ with $\Gamma = \frac{\varepsilon_{ice}+1}{\varepsilon_{ice}+2}\frac{n_{wh}}{n_i} + \frac{4\pi\alpha_M n_m}{3}$



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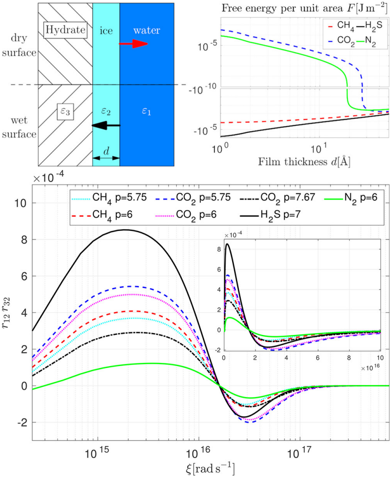
- Product of reflection coefficients

$$r_{12}r_{32} = \frac{\varepsilon_H - \varepsilon_{ice}}{\varepsilon_H + \varepsilon_{ice}}\frac{\varepsilon_W - \varepsilon_{ice}}{\varepsilon_W + \varepsilon_{ice}}$$



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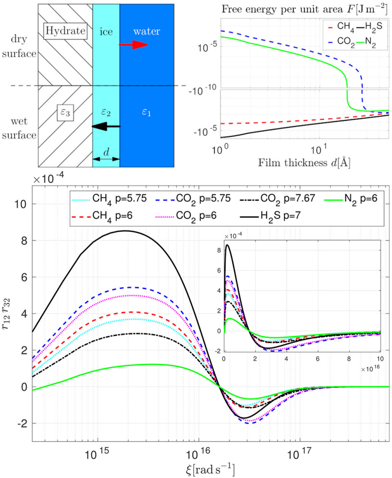
- Stable ice layers for CO_2 and N_2 hydrates of 3-4 nm thickness



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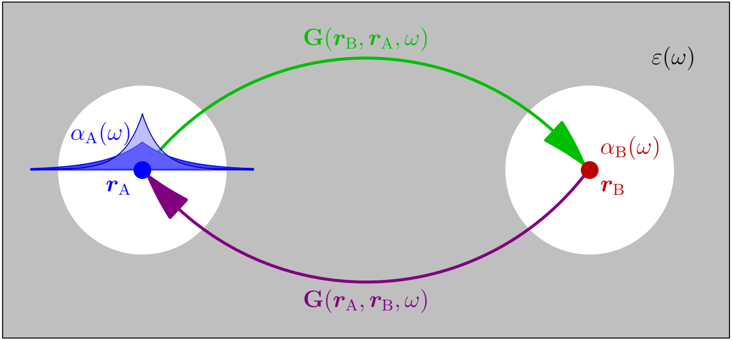
Effects of a solvent



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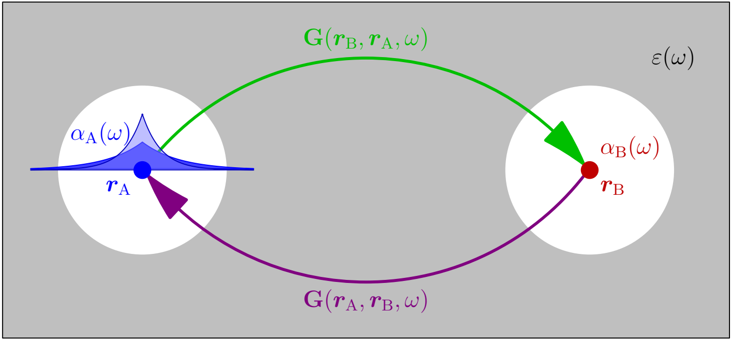

Screening of wave function restricts volume V^{res}: $\alpha \to \alpha \frac{V^{\mathrm{res}}}{V^{\mathrm{free}}}$

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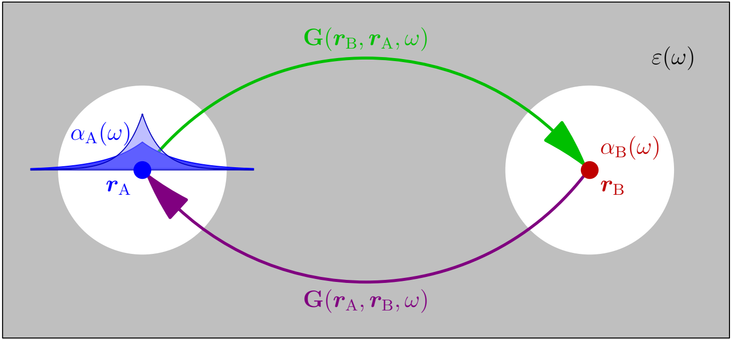

Screening of wave function restricts volume V^res: $\alpha \to \alpha \frac{V^\mathrm{res}}{V^\mathrm{free}}$

Transmission through boundaries cavity models $\alpha \to \alpha^*$

Absorption via propagation ???

Screened non-retarded vdW

$$U_{\mathrm{vdW}}(d) = -\frac{C_6^\star}{d^6}\,, \quad C_6^\star = \frac{3\hbar}{16\pi^3\varepsilon_0^2}\int\limits_0^\infty \frac{\alpha_{\mathrm{A}}^\star(i\xi)\alpha_{\mathrm{B}}^\star(i\xi)}{\varepsilon^2(i\xi)}\mathrm{d}\xi$$

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- Can we find away to approximate $C_6^\star$ with the free-space $C_6 = \frac{3\hbar}{16\pi^3\varepsilon_0^2}\int\limits_0^\infty \alpha_\mathrm{A}(i\xi)\alpha_\mathrm{B}(i\xi)\mathrm{d}\xi$?

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- Single-point Gauss quadrature rule $I = \int_0^\infty f(x)g(x)\mathrm{d}x \approx f(x_0)m_0$

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- Series of momenta $I_i = \int_0^\infty x^i g(x)\mathrm{d}x \to m_0 = I_0$ and $x_0 = I_1/I_0$

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$$\overline{\omega} = \frac{\int_0^\infty \xi\alpha_{\mathrm{A}}(i\xi)\alpha_{\mathrm{B}}(i\xi)\mathrm{d}\xi}{\int_0^\infty \alpha_{\mathrm{A}}(i\xi)\alpha_{\mathrm{B}}(i\xi)\mathrm{d}\xi}$$

Averaged mean-frequencies

TABLE I. Average main-frequencies $\overline{\omega}$ (eV) for different molecule pairs. The corresponding parameters for the polarizabilities are taken from Refs. 18 and 40.

	CH_4	NO_2	CO_2	CO	N_2O	O_3	O_2	N_2	H_2S	NO
CH_4	11.4	12.6	12.6	12.2	12.3	12.7	13.2	12.8	10.3	12.8
NO_2	12.6	14.2	14.3	13.7	13.9	14.4	15.0	14.4	11.3	14.5
CO_2	12.6	14.3	14.3	13.7	14.0	14.4	15.0	14.4	11.4	14.5
CO	12.2	13.7	13.7	13.1	13.4	13.8	14.4	13.8	11.0	13.9
N_2O	12.3	13.9	13.9	13.4	13.6	14.0	14.7	14.0	11.1	14.1
O_3	12.7	14.4	14.4	13.8	14.0	14.5	15.2	14.4	11.4	14.6
O_2	13.2	15.0	15.0	14.4	14.7	15.2	15.9	15.1	11.9	15.2
N_2	12.8	14.4	14.4	13.8	14.0	14.5	15.1	14.4	11.5	14.6
H_2S	10.3	11.3	11.4	11.0	11.1	11.4	11.9	11.5	9.3	11.5
NO	12.8	14.5	14.5	13.9	14.1	14.6	15.2	14.6	11.5	14.7

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CO	12.2	13.7	13.7	13.1	13.4	13.8	14.4	13.8	11.0	13.9
N_2O	12.3	13.9	13.9	13.4	13.6	14.0	14.7	14.0	11.1	14.1
O_3	12.7	14.4	14.4	13.8	14.0	14.5	15.2	14.4	11.4	14.6
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- Typically larger than 10 eV

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CO	12.2	13.7	13.7	13.1	13.4	13.8	14.4	13.8	11.0	13.9
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N_2	12.8	14.4	14.4	13.8	14.0	14.5	15.1	14.4	11.5	14.6
H_2S	10.3	11.3	11.4	11.0	11.1	11.4	11.9	11.5	9.3	11.5
NO	12.8	14.5	14.5	13.9	14.1	14.6	15.2	14.6	11.5	14.7

- Typically larger than 10 eV
- Approximation: $\varepsilon(i\overline{\omega}) \approx \mathrm{Re}\,\varepsilon(\overline{\omega})$

Screening effects

[1] JF *et al. Effective screening of medium-assisted van der Waals interactions between embedded particles*, J. Chem. Phys. **154**, 104102 (2021).

Screening effects

- Screened vdW $U_{\mathrm{vdW}}(d) = -\frac{C_6^\star}{d^6}$ with

$$C_6^\star = \frac{C_6}{[\mathrm{Re}\,\varepsilon(\overline{\omega})]^2} \left(\frac{V^{\mathrm{res}}}{V^{\mathrm{free}}}\right)_A \left(\frac{V^{\mathrm{res}}}{V^{\mathrm{free}}}\right)_B$$

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- Screened Coulomb $U_{\mathrm{el}}(d) = \frac{1}{4\pi\varepsilon_0\varepsilon(0)} \frac{Q}{d}$

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- Screened Coulomb $U_{\mathrm{el}}(d) = \frac{1}{4\pi\varepsilon_0\varepsilon(0)} \frac{Q}{d}$
- Interesting fact about water: $\varepsilon(0) \approx 80$ and $[\mathrm{Re}\,\varepsilon(\overline{\omega})]^2 \approx 2$
  $\rightarrow$ Screening of Coulomb force 40 times stronger than screening of vdW forces

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Summary

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- Introduced concepts of macroscopic Quantum Electrodynamics

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