Lecture 10. The Dispersion Force and van der Waals Interaction

Last Lecture:

- Intermolecular interactions are contributed by charge (q), dipole (u) and induced dipole (α)

- Following interactions have power law r^{-6}:

    - Keesom: u-u

    - Debye: u-α

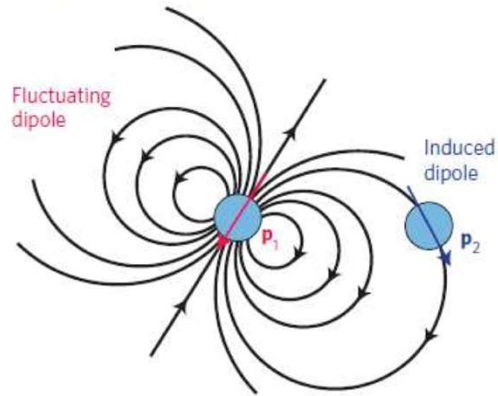   - London dispersion: α-α

→This lecture will discuss about the "elusive" dispersion interaction

Perspectives:

- What us the origin of the interaction between non-polar molecules?

- How is the dispersion interaction compared with the other types of interaction

- Can you engineer such forces / interactions?

Interaction between Nothing and Dancing Charges:
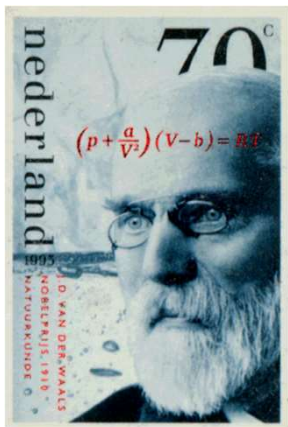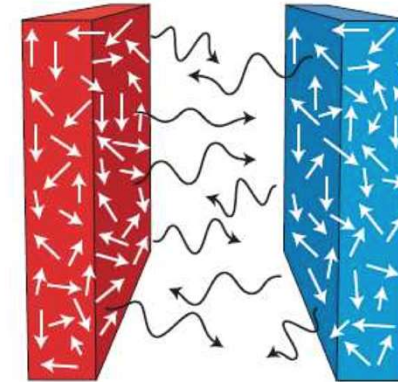# A Brief History of vdW-Casimir Effect
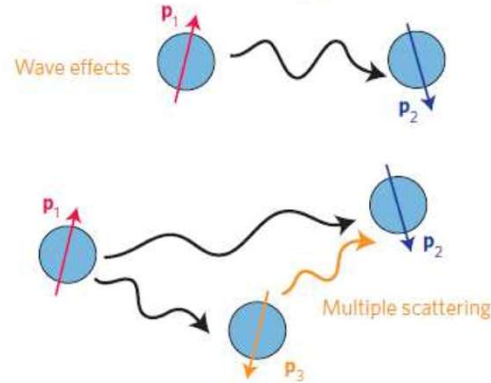
J.D. van der Waals
1873

Fritz London
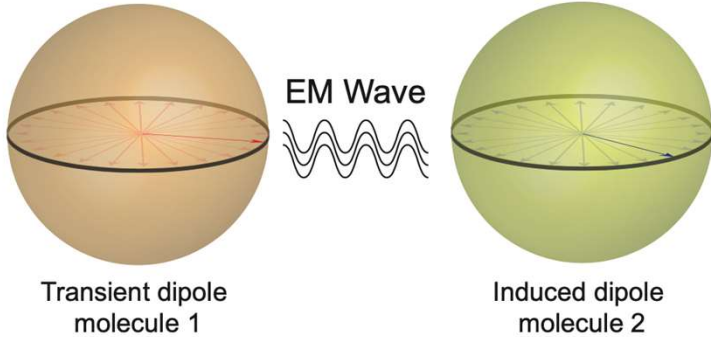1930

Hendrik Casimir
1948

Dirk Polder
1948

Evgeny Lifshitz
1954

Semi-Classical Theory of London Dispersion

Interactions between transient dipole moments of Bohr atoms

$$U_1 = a_c \cdot e \rightarrow W_{u\alpha} = \frac{-u^2 \alpha_{02}}{(4\pi\varepsilon_c\varepsilon_r)^2 r^6}$$

EM Wave

Transient dipole
molecule 1

Induced dipole
molecule 2

Interaction **Free** Energy (half of internal):

$$w_{\alpha\alpha}(r) = -\frac{(ea_0)^2 \alpha_{02}}{(4\pi\varepsilon_0\varepsilon_r)^2 r^6}$$

$$\alpha_{01} = 4\pi\varepsilon_0 a_0^3$$
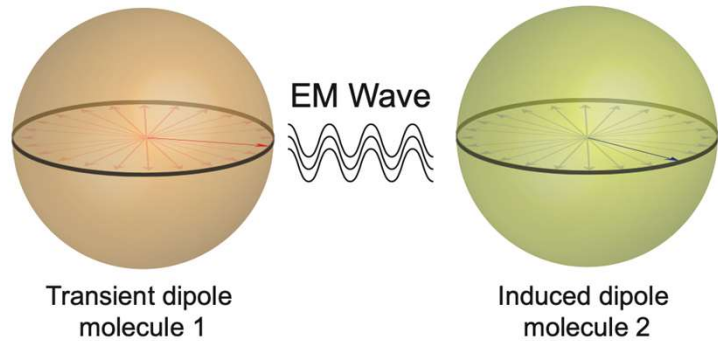
Val of e⁻-cloud

$$= \frac{-e^2}{4\pi\varepsilon_c \cdot a_0} \cdot \frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_c\varepsilon_r)^2 r^6}$$

↳ Ionization energy of Bohr atom

$$h\nu_I = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 a_0} = 13.6eV$$

Semi-Classical Theory of London Dispersion

Interactions between transient dipole moments of Bohr atoms

$$\omega_{\alpha\alpha} = -2\,h\,\nu_{\wedge}\cdot\frac{\alpha_{01}\,\alpha_{02}}{(4\pi\varepsilon_0\varepsilon_r)^2\,r^6}$$

EM Wave

Transient dipole
molecule 1

Induced dipole
molecule 2

London free energy dispersion:

$$w_{\alpha\alpha} = -\frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0\varepsilon_r)^2 r^6}\frac{h\nu_{I1}\nu_{I2}}{\nu_{I1}+\nu_{I2}}$$
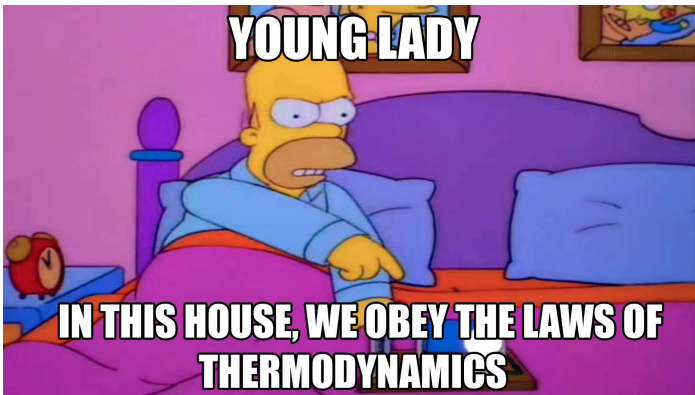
→ harmonic mean

⟹ Semi-classical approach is close to real expression

Unifying All Components of vdW Interactions

Free Iinteraction Energy:

$$w_{\text{vdW}} = -\underbrace{\frac{u_1^2 u_2^2}{3k_B T (4\pi\varepsilon_0\varepsilon_r)^2 r^6}}_{\text{Keesom}} - \underbrace{\frac{u_1^2 \alpha_{02} + u_2^2 \alpha_{01}}{(4\pi\varepsilon_0\varepsilon_r)^2 r^6}}_{\text{Debye}} - \underbrace{\frac{3\alpha_{02}\alpha_{01}\frac{h\nu_1\nu_2}{\nu_1+\nu_2}}{2(4\pi\varepsilon_0\varepsilon_r)^2 r^6}}_{\text{London}}$$

$$= -\frac{\beta_{\text{Keesom}} + \beta_{\text{Debye}} + \beta_{\text{London}}}{r^6}$$

$$w_{\alpha\alpha} = \frac{-3k_B T\, \alpha_{01}\, \alpha_{02}}{(4\pi\varepsilon_c\varepsilon_r)^2 r^6}$$

$$(300K) \begin{cases} k_B T \simeq 0,026\,eV \\ h\nu \simeq 13,6\,eV \end{cases}$$

YOUNG LADY

IN THIS HOUSE, WE OBEY THE LAWS OF THERMODYNAMICS

Strengh of London Dispersion Interactions

Melting point T_m of Nobel gases

σ
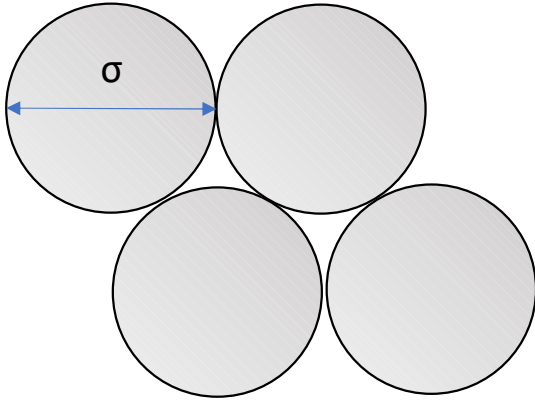
$q = 0, \quad u = 0, \quad \alpha = \alpha_0$

Critical condition :

$$vdW + thermal = 0$$
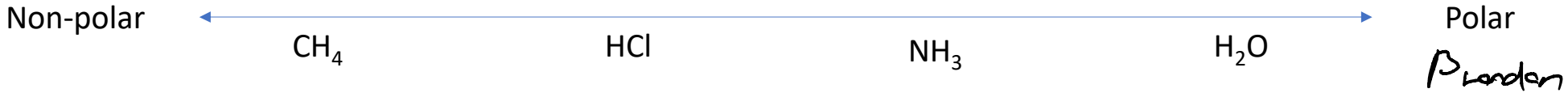
$$\Rightarrow \quad \omega_{vdW} + E_{kin} = 0$$

$$\Rightarrow \quad -\frac{3}{4} \frac{\alpha_0^2}{(4\pi s_0)} \cdot \frac{1}{\sigma^6} \cdot h\gamma_{\Xi} + \frac{3}{2} k_B T = 0$$

$$\alpha_0 = 4\pi s_0 \left(\frac{\sigma}{2}\right)^3$$

$\Rightarrow$ T_m is independent of radis σ!

	Calc. T_m	Exp. T_m
Eg:		
Ne	22K	27K
Ar	85K	87K

Comparison Between Dispersion Interactions vs Keesom / Debye Interactions

Non-polar ←———————————————————————————→ Polar

CH_4 HCl NH_3 H_2O

Proportionality of dispersion interaction: $\eta_{London} = \dfrac{\beta_{London}}{\beta_{London} + \beta_{Keesom} + \beta_{Debye}}$

	β_{vdW} (10^{-79} J · m^6)	η_{London}
CH_4 - CH_4	102 ⎫ Similar	100 %
HCl - HCl	123 ⎬	86 %
NH_3 - NH_3	111	57 % ⎫ More dipoles
H_2O - H_2O	139 ⎭	24 % ⎭

⟹ non neglectable

Revisit of Old Equations

Recall Lecture 1: $A_{AB} = \sqrt{A_{AA} A_{BB}}$

$\longrightarrow$ Hamaker const: $A_{AB} = \pi^2 \beta_{AB} \cdot S_A \cdot S_B$

If **ONLY** London dispersion:

$$\beta_{AB} \propto \alpha_{oA} \cdot \alpha_{oB} \cdot \frac{h^2 \nu_1 \cdot \nu_2}{h\nu_2 + h\nu_2} \underset{(\nu_1 \simeq \nu_2)}{\sim} \alpha_{oA} \cdot \alpha_{oB} \sqrt{h\nu_1 \cdot h\nu_2}$$

$$\beta_{AA} \propto \alpha_{oA}^2 \, h\nu_1 \quad, \quad \beta_{BB} \propto \alpha_{oB}^2 \cdot h\nu_2$$

$$\beta_{AB} = \sqrt{\beta_{AA} \cdot \beta_{BB}}$$

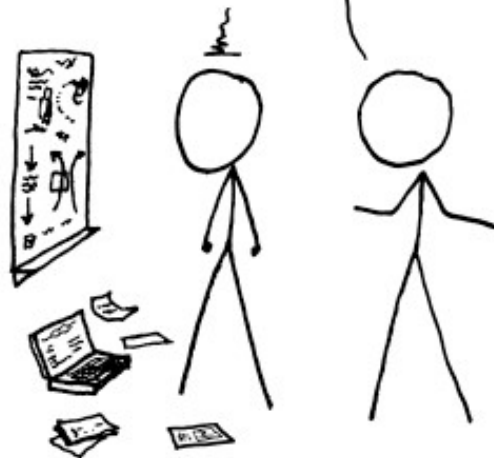$$\longrightarrow A_{AB} = \sqrt{A_{AA} A_{BB}}$$

holds for system ONLY with London dispersion

$\Longrightarrow$ does not work for highly polar system

YOU'RE TRYING TO PREDICT THE BEHAVIOR OF <COMPLICATED SYSTEM>? JUST MODEL IT AS A <SIMPLE OBJECT>, AND THEN ADD SOME SECONDARY TERMS TO ACCOUNT FOR <COMPLICATIONS I JUST THOUGHT OF>.

EASY, RIGHT?

SO, WHY DOES <YOUR FIELD> NEED A WHOLE JOURNAL, ANYWAY?

LIBERAL-ARTS MAJORS MAY BE ANNOYING SOMETIMES, BUT THERE'S *NOTHING* MORE OBNOXIOUS THAN A PHYSICIST FIRST ENCOUNTERING A NEW SUBJECT.

Modern Theory of Dispersion Interactions – Frequency Dependency

Why is the coefficient of $w_{\alpha\alpha}$ different? → Time in Electrodynamics instead of Electrostatics!

$h\nu$ $k_B T$
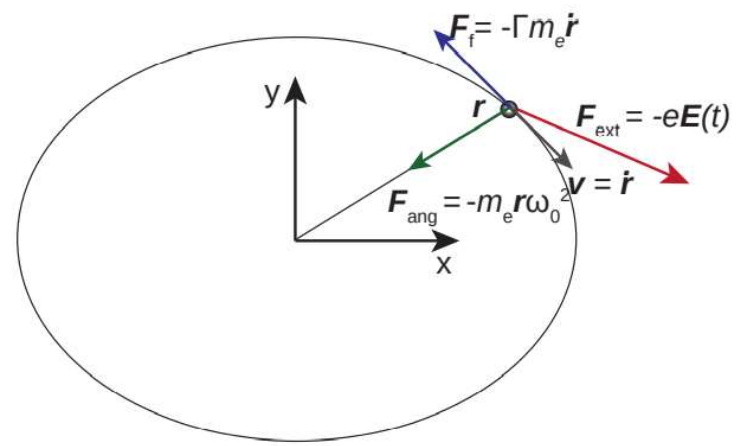
Lorentz Oscillator Model

Equation of motion: $\quad m_e\ddot{\mathbf{r}} + \Gamma m_e\dot{\mathbf{r}} + m_e\omega_0^2\mathbf{r} = -e\mathbf{E}$

↳ Dampening factor

Fourier trafo

$\Rightarrow m_e\hat{\mathbf{r}}(\omega)(-\omega^2 + i\Gamma\omega + \omega_0^2) = -e\hat{\mathbf{E}}$

$F_f = -\Gamma m_e\dot{\mathbf{r}}$

$\mathbf{r}$ $F_{ext} = -e\mathbf{E}(t)$

$F_{ang} = -m_e\mathbf{r}\omega_0^2$ $\mathbf{v} = \dot{\mathbf{r}}$

$$\alpha_0 = \alpha(\omega = 0) = \frac{e^2}{m_e\omega_0^2}$$
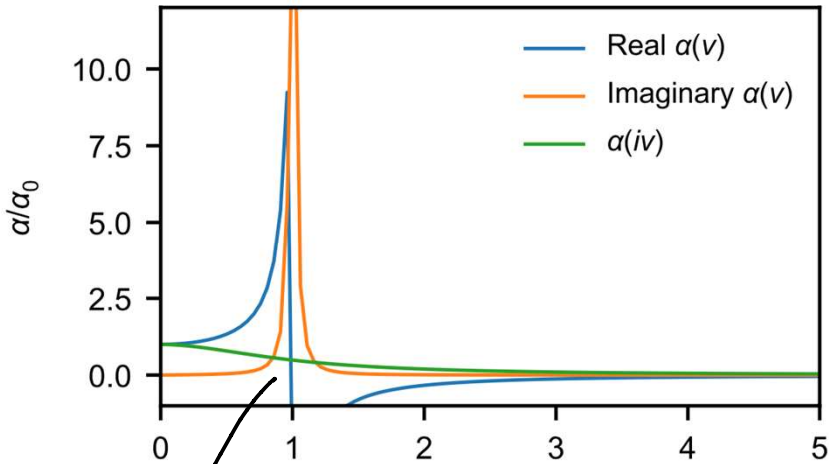
ω_0: Oscillating freq $\simeq 2\pi \cdot \nu_I$

$$\alpha(\omega) = \frac{-e\hat{\mathbf{r}}(\omega)}{\hat{\mathbf{E}}(\omega)} = \frac{\alpha_0}{1 + i\Gamma\left(\frac{\omega}{\nu_0}\right) - \left(\frac{\omega}{\omega_0}\right)^2} = \frac{\alpha_0}{1 + \Gamma\left(\frac{i\nu}{\nu_I}\right) + \left(\frac{i\nu}{\nu_I}\right)^2} = \alpha(i\nu)$$
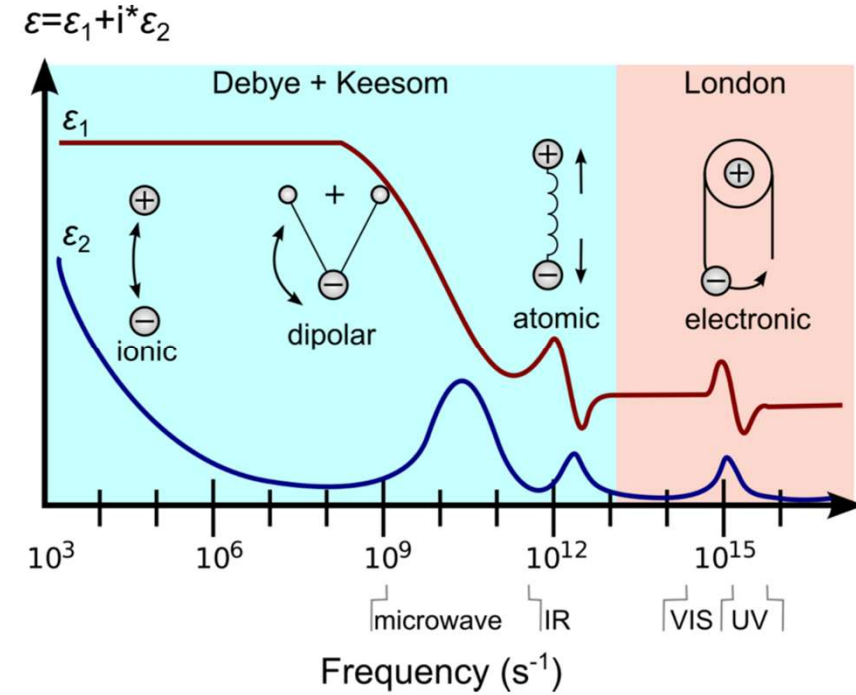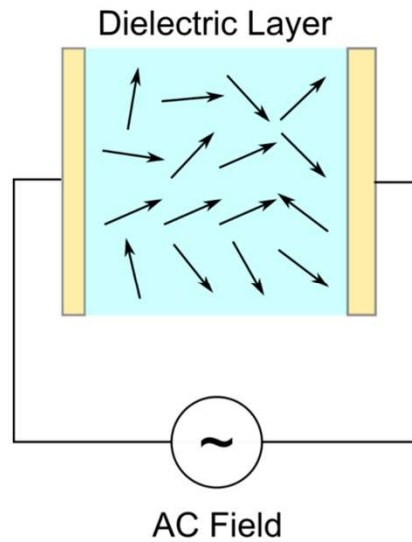
↳ phase

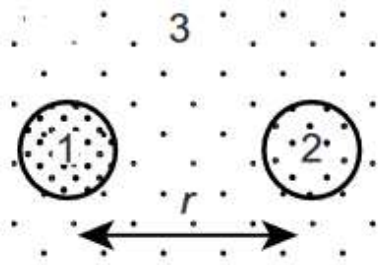# Modern Theory of Dispersion Interactions – Frequency Dependency

$$\varepsilon = \frac{E_{ext}}{E_{int}}$$

monotonically

Dielectric Layer

AC Field

$\varepsilon = \varepsilon_1 + i*\varepsilon_2$

Debye + Keesom

London

ε_1

ε_2

ionic   dipolar   atomic   electronic

10^3 10^6 10^9 10^{12} 10^{15}

microwave   IR   VIS   UV

Frequency (s^{-1})

Modern Theory of Dispersion Interactions – McLachlan Model

McLachlan Model (microscopic)

$$w_{\mathrm{vdW}}(r) = -\frac{6k_{\mathrm{B}}T}{(4\pi\varepsilon_0)^2 r^6} \sum_{n=0}^{\infty} \frac{\alpha_1(i\nu_n)\alpha_2(i\nu_n)}{\varepsilon_3^2(i\nu_n)}$$
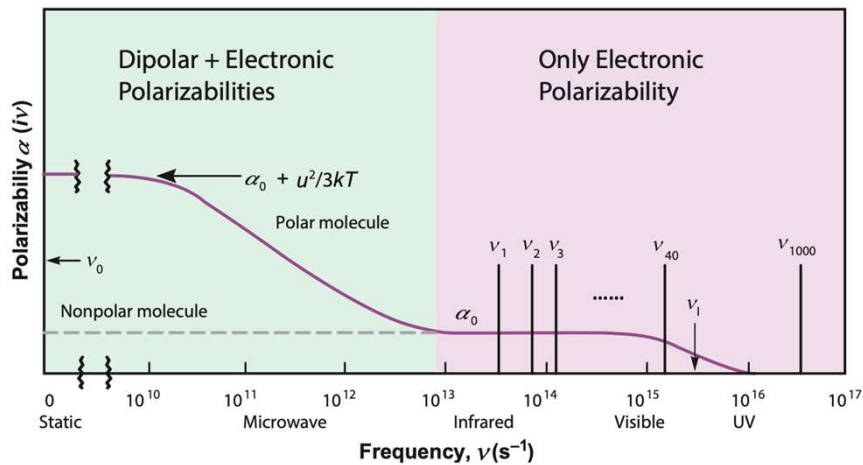
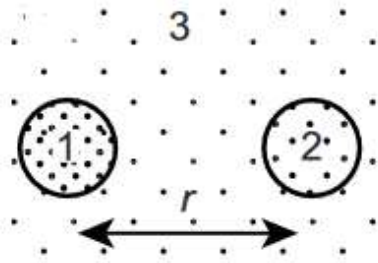$\frac{1}{2}$ if $n=0$

ν_n : Matsubara Frequency

$h\nu_n = 2\pi k_{\mathrm{B}} \cdot T \cdot n$

$h\nu_1 = 0.16\,eV$ $(300\,K)$

$\begin{cases} n=0 \quad \text{Debye} + \text{Keesom} + \text{0th London} \\ n \gtrsim 1 \quad \text{London} \end{cases}$

Modern Theory of Dispersion Interactions – McLachlan Model
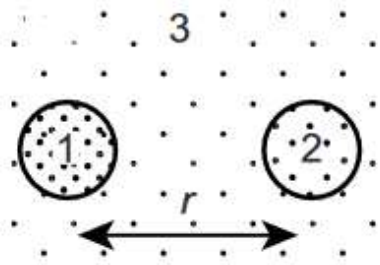

$n = 0$

$$w_{\mathrm{vdW}}(r) = -\frac{6k_{\mathrm{B}}T}{(4\pi\varepsilon_0)^2 r^6} \sum_{n=0}^{\infty} {}' \frac{\alpha_1(i\nu_n)\alpha_2(i\nu_n)}{\varepsilon_3^2(i\nu_n)}$$

$$w_{\mathrm{vdW}}(\nu = 0, r) = -\frac{1}{2}\frac{6k_{\mathrm{B}}T(\alpha_{01} + u_1^2/(3k_{\mathrm{B}}T))(\alpha_{02} + u_2^2/(3k_{\mathrm{B}}T))}{(4\pi\varepsilon_0\varepsilon_3^2)^2 r^6}$$

$$= -\underbrace{\frac{u_1^2 u_2^2}{3k_{\mathrm{B}}T(4\pi\varepsilon_0\varepsilon_3)^2 r^6}}_{\text{Keesom}} - \underbrace{\frac{u_1^2\alpha_{02} + u_2^2\alpha_{01}}{(4\pi\varepsilon_0\varepsilon_3)^2 r^6}}_{\text{Debye}} - \underbrace{\frac{3k_{\mathrm{B}}T\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0\varepsilon_3)^2 r^6}}_{\text{London}(n=0)}$$

Modern Theory of Dispersion Interactions – McLachlan Model

$$n \geq 1 \qquad , \qquad \sum \to \int \quad , \quad h\nu_n = 2\pi k_B T n$$

$$\Rightarrow h\,d\nu = 2\pi k_B T\, dn$$

$$\Rightarrow \omega_{vdw}\,(n \geq 1) = \frac{h}{2\pi}\,\frac{6}{(4\pi \varepsilon_0 \varepsilon r)^2} \int_{\nu_I}^{\infty} \alpha_1(i\nu)\,\alpha_2(i\nu)\,d\nu$$

$$\left\{ \begin{array}{l} \text{Replace the lower limit } \nu_I \simeq 0 \\[6pt] \alpha(i\nu) = \dfrac{\alpha}{1 + \left(\frac{i\nu}{\nu_I}\right)^2} \\[6pt] \varepsilon_3 = 1 \end{array} \right.$$

$$\Rightarrow \omega_{vdw}\,(n \geq 1) = -\frac{3}{2}\,\frac{\alpha_{01}\,\alpha_{02}}{(4\pi \varepsilon_0 \varepsilon r)^2\, r^6}\,\frac{h\nu_{I1} \cdot \nu_{I2}}{h\nu_{I1} + h\nu_{I2}}$$

London Dispersion

McLachlan Model: Revisiting Previous Questions

1. Coefficients of dispersion interactions

Lecture 9 $\rightarrow$ electrostatics $\rightarrow$ $\omega_{dd} \propto k_B T$

Today $\rightarrow$ electrodynamics $\rightarrow$ $\omega_{dd} \propto h\nu_I$

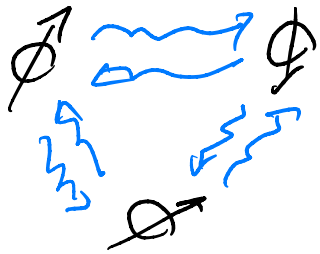$\Rightarrow$ Dispersion dominates at range Vis $-$ UV

2. Why *Dispersion?*

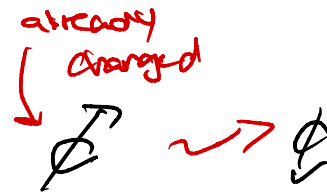1. $\alpha \cdot \varepsilon$ dependent on freq.

2. Vis $-$ UV range strongest

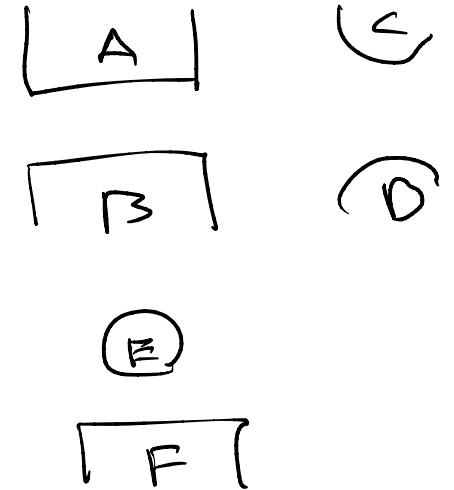# Macroscopic Many-body vdW – Lifshitz Theory

Some drawbacks of London theory:

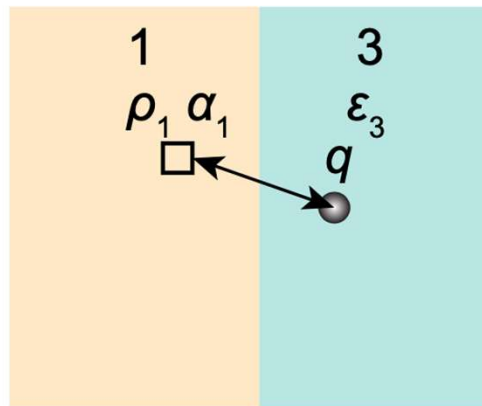Lack of many-body effect   Retardation Effect   Geometric Uniformity

Hamaker Constant in Lifshitz Theory
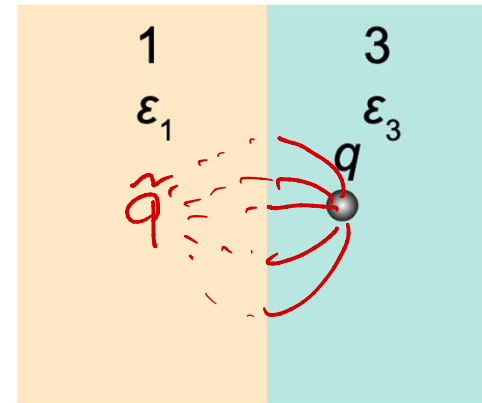
McLachlan Eqs –> Bulk system: Naïve approach

Microscopic approach
$w_{q1} = f(\rho, \alpha, \varepsilon_3)$

Macroscopic approach
$w_{q1} = f(\varepsilon_1, \varepsilon_3)$

$$w_{q1} = \int_{\delta}^{\infty} dx \int_{0}^{\infty} w_{q\alpha}(r = \sqrt{(x^2 + y^2)})\rho_1(2\pi y)dy$$

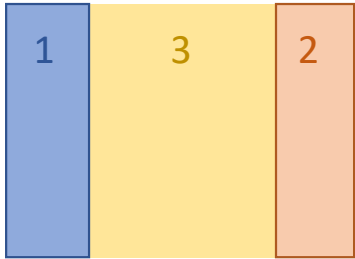$$= -\frac{\pi q^2 \rho_1 \alpha_1}{(4\pi\varepsilon_0\varepsilon_3)^2\delta}$$

$$w_{q1} = -\frac{q^2}{(4\pi\varepsilon_0)\varepsilon_3(2\delta)}\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}$$

$$\rho_1 \alpha_1 = 2\varepsilon_0\varepsilon_3 \cdot \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}$$

Hamaker Constant in Lifshitz Theory

$$A_{132} = \frac{3kT}{2} \sum_{n=0}^{\infty}{}' \left[\frac{\varepsilon_1(i\nu_n) - \varepsilon_3(i\nu_n)}{\varepsilon_1(i\nu_n) + \varepsilon_3(i\nu_n)} \right] \left[\frac{\varepsilon_2(i\nu_n) - \varepsilon_3(i\nu_n)}{\varepsilon_2(i\nu_n) + \varepsilon_3(i\nu_n)} \right]$$

$$\underbrace{\qquad}_{\Delta_{13}} \qquad \underbrace{\qquad}_{\Delta_{23}}$$

Case

1.) $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 \implies A_{132} = 0$

2.) $\varepsilon_3 = 1$ $\qquad \Delta_{13} = \dfrac{\varepsilon_1 - 1}{\varepsilon_1 + 1} > 0$

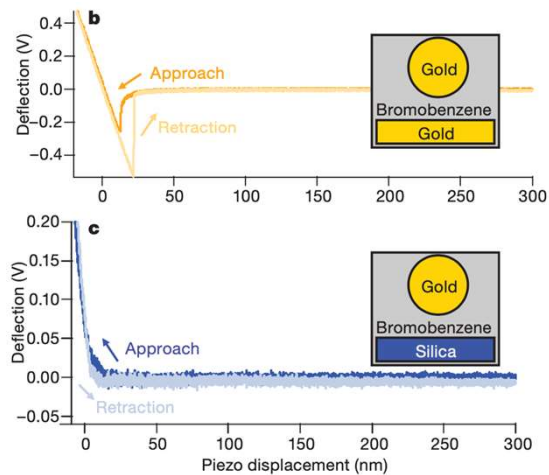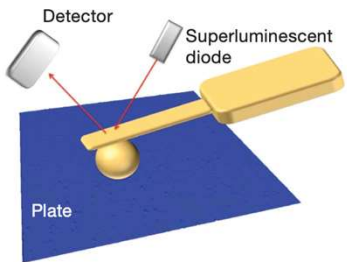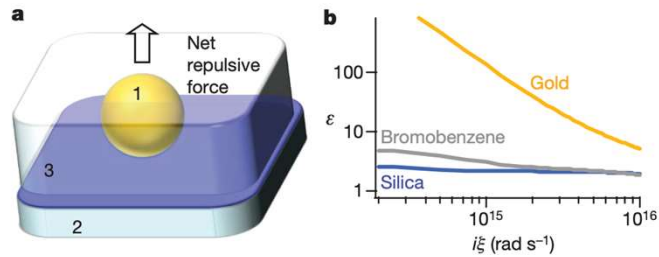$\Delta_{23} \, | > 0$

$\implies$ attraction

3.) $\varepsilon_1 > \varepsilon_3 > \varepsilon_2 \implies$ repulsive interaction

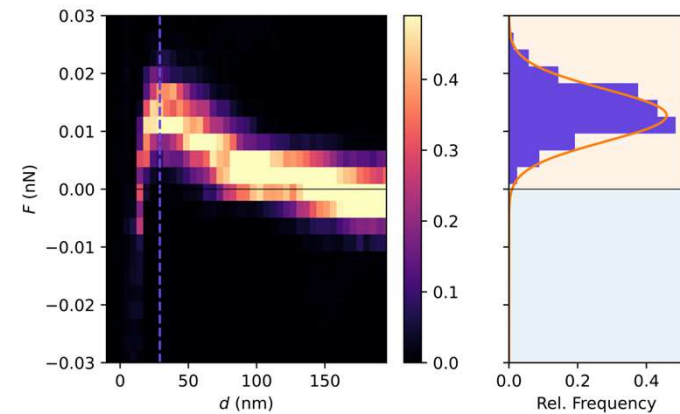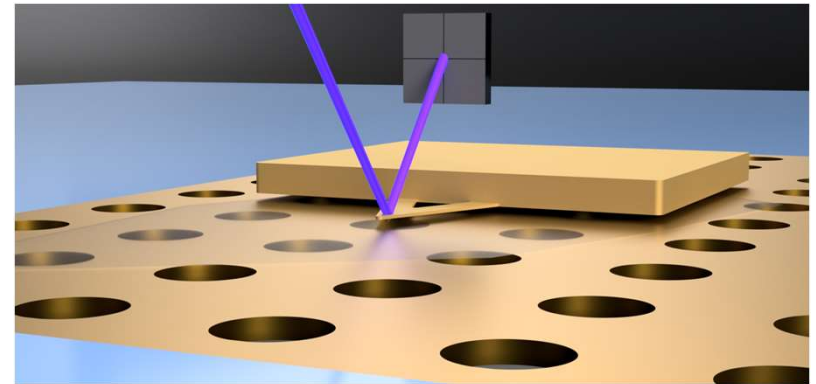# Can van der Waals Interaction Be Repulsive?

If the dielectric functions ε_1 ε_2 ε_3 of materials 1, 2 and medium 3 form cascade.
 i.e. $\varepsilon_1 < \varepsilon_3 < \varepsilon_2$

Repulsive long-range Casimir interactions in liquid

vdW interaction mediate by 2D-Materials

Munday, et al. Nature 457, 170–173 (2009).

Preliminary Work