

## Homework Assignment 3

Due date: 26.April.2024

In this homework assignment, we will solve several questions involving interfacial transport phenomena that can be answered based on our knowledge from Lectures 9 - 11.

### Q1 Understand the Lifshitz Theory of vdW Interactions

In Lecture 10 we have briefly discussed the modern version of the van der Waals interaction – the Lifshitz theory.

Here, we have some hands-on exercises on how to apply such theories to study the vdW interactions. For your reference, the Hamaker constant  $A_{123}$  between two macroscopic bodies 1 and 2 in medium 3 separated by distance  $d$  (see Figure 1), is approximated as:

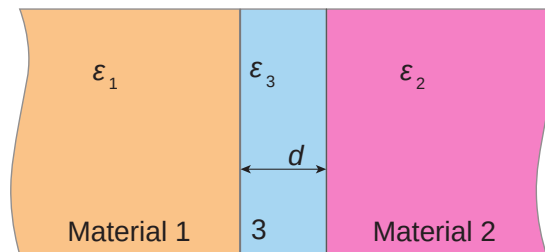


Figure 1: Scheme of macroscopic bodies 1 and 2 in medium 3.

$$A_{132} = \frac{3k_B T}{2} \sum_{n=0}^{\infty} \left[ \frac{\varepsilon_1(i\nu_n) - \varepsilon_3(i\nu_n)}{\varepsilon_1(i\nu_n) + \varepsilon_3(i\nu_n)} \right] \left[ \frac{\varepsilon_2(i\nu_n) - \varepsilon_3(i\nu_n)}{\varepsilon_2(i\nu_n) + \varepsilon_3(i\nu_n)} \right] \quad (1)$$

where  $\nu_n$  is the  $n$ -th Matsubara frequency such that  $h\nu = 2\pi k_B T n$ , and  $\varepsilon_j$  is the frequency-dependent relative permittivity (dielectric function) of material  $j$ . The prime (') indicates a pre-factor of 1/2 to the summation term at  $n = 0$ . For simplicity we use the notation  $\Delta_{jk} = \frac{\varepsilon_j - \varepsilon_k}{\varepsilon_j + \varepsilon_k}$  for the dielectric mismatch between two materials throughout the context.

### Temperature dependency of Hamaker constant

It may seem that  $A_{132}$  in Eq. 1 increases with  $T$ . This is not physical since we know that  $A_{123}$  cannot diverge when  $T \rightarrow \infty$ , and there is still vdW force even when  $T = 0$  K. To analyze this discrepancy, let's take the following steps:

1. Assume that  $\epsilon$  does not depend on the temperature  $T$ , and can be regarded as constant within a small frequency range ( $\nu_{\text{low}}, \nu_{\text{high}}$ ). Show that the contribution to the Hamaker constant within this energy range

$$\frac{3k_B T}{2} \sum_{\nu_n \geq \nu_{\text{low}}}^{\nu_n \leq \nu_{\text{high}}} \Delta_{13}(i\nu_n) \Delta_{23}(i\nu_n) \quad (2)$$

does not depend on  $T$

2. Let's consider a toy-model for the dielectric function of material (labeled as a). Similar to the frequency-dependent polarizability, the frequency-dependent  $\epsilon$  in the single-oscillator Lorentz model has the form:

$$\epsilon_a(i\nu) = 1 + \frac{f_{\text{osc}}}{1 + \left(\frac{\nu}{\nu_{\text{osc}}}\right)^2} \quad (3)$$

where  $\nu_{\text{osc}}$  is the resonance frequency of the oscillator the  $f_{\text{osc}}$  is the oscillation strength. Use Eq. 3 to plot  $\epsilon(i\nu)$  of as a function of  $\nu$  of a material that has refractive index  $n = 1.53$  and  $h\nu_{\text{osc}} = 10$  eV. Note that the refractive index  $n = \sqrt{\epsilon_a(\nu = 0)}$ .

3. Now plug your model  $\epsilon_a$  of Q2.2 into Eq. 1 to calculate the Hamaker constant  $A_a$  in vacuum. In other words, we have materials 1, 2 = a, and 3 = vacuum. Show how  $A_a$  changes with the temperature  $T$ . Does your plot agree with the assumption in Q2.1 <sup>1</sup>?

### Lifshitz Model for Real Materials

4. In order to apply the Lifshitz model to real materials, we need to obtain the dielectric profile  $\epsilon(i\nu)$  of each material from experimental data. In practice, it is much easier to measure, rather than compute, the optical absorption coefficient (also known as the *imaginary* permittivity  $\epsilon''$  <sup>2</sup>) The conversion between  $\epsilon''(\omega)$  on real frequency and  $\epsilon(i\nu)$  is done via the Kramers-Kronig relations (KKR):

$$\epsilon(i\nu) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon''(\omega)}{\omega^2 + \nu^2} d\omega \quad (4)$$

As an example, we provide you the  $\epsilon''(\omega)$  values of 3 different materials: silica ( $\text{SiO}_2$ ), bromobenzene (BrPh) and gold (Au) in the attachment `eps-data.zip`. Use Eq. 4 to compute frequency-dependent  $\epsilon(i\nu)$  of each material and compare them in the same figure. You should see  $\epsilon_{\text{SiO}_2} < \epsilon_{\text{BrPh}} < \epsilon_{\text{Au}}$  when  $h\nu < 4$  eV.

5. Use your results in Q2.4 to calculate the Hamaker constant  $A_{132}$  where 1 =  $\text{SiO}_2$ , 2 = Au and 3 = BrPh. You will find  $A_{132}$  is still positive (attractive interaction). Explain this by plotting the frequency-dependent contribution  $G(\nu_n)$  to the Hamaker constant, such that:

$$G(\nu_n) = f(n) \cdot \frac{3k_B T}{2} \Delta_{13}(i\nu_n) \Delta_{23}(i\nu_n) \quad (5)$$

$$f(n) = \begin{cases} \frac{1}{2} & n = 0 \\ 1 & n > 0 \end{cases}$$

<sup>1</sup>In reality, the temperature dependency of  $\epsilon$  cannot be ignored.

<sup>2</sup>Actually the imaginary part of the *complex* permittivity  $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$  on *real* frequency  $\omega$ .

## Explaining Repulsive vdW-Casimir Interactions by Lifshitz Theory

Is it possible to harness repulsive interactions in the SiO<sub>2</sub>-BrPh-Au system? Yes. In fact, due to the limited speed of light, when the characteristic time  $\tau$  of electromagnetic (EM) wave traveling between two macroscopic bodies is much longer than the intrinsic time scale of EM-wave oscillation (i.e.  $\omega^{-1}$  where  $\omega = 2\pi\nu$  is the angular frequency of the EM wave), the interaction can be significantly suppressed (retarded). The full Lifshitz theory seamlessly bridges the vdW (non-retarded) and Casimir (retarded) interactions<sup>3</sup>.

6. When do we need to consider the retardation effect? Please qualitatively compare the following scenarios:

- a)  $h\nu = 0.1 \text{ eV}, d = 0.5 \text{ nm}$
- b)  $h\nu = 50 \text{ eV}, d = 0.5 \text{ nm}$
- c)  $h\nu = 0.1 \text{ eV}, d = 50 \text{ nm}$
- d)  $h\nu = 50 \text{ eV}, d = 50 \text{ nm}$

7. The retardation effect makes the Hamaker “constant” actually dependent on the separation  $d$ . A simplified expression for the interaction energy between macroscopic bodies 1 and 2 over medium 2,  $\Phi_{132}(d)$ , using the retarded Lifshitz theory, is given by the following equation set:

$$\begin{aligned}\Phi_{132}(d) &= -\frac{A_{132}(d)}{12\pi d^2} & (6) \\ A_{132}(d) &= \frac{3k_B T}{2} \sum_{n=0}^{\infty} \Delta_{13}(i\nu_n) \Delta_{23}(i\nu_n) R_n \\ R_n &= (1 + r_n) e^{-r_n} \\ r_n &= \frac{4\pi d \sqrt{\epsilon_3(i\nu_n)}}{c} \nu_n\end{aligned}$$

where  $c$  is the speed of light in vacuum and  $\nu_n$  is the  $n$ -th Matubara frequency. In brief, the distance-dependent Hamaker constant  $A_{132}(d)$  just superimposes a retardation coefficient  $R_n$  onto the non-retarded expression (see Eq. 1).  $R_n$  is further dependent on the separation  $d$  and frequency  $\nu_n$ . Please plot the pressure (force per area) between the macroscopic bodies  $F_{132}(d)$  as function of  $d$ , which is calculated by:

$$F_{132}(d) = -\frac{\partial \Phi_{132}(d)}{\partial d} \quad (7)$$

Notice that the derivative may be computed numerically. Do you see a repulsive energy / pressure when  $d > 20 \text{ nm}$ ? Propose a practical setup that may be used to measure the repulsive interactions.

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<sup>3</sup>See Parsegian, *Van der Waals Forces: A Handbook for Biologists, Chemists, Engineers, and Physicists*. Cambridge Press (2010), Chapter 2.3

## Q2 Realistic Picture of Electric Double Layer

In Lecture 11 we learn about the formation of an electric double layer (EDL) when a charged plate is inserted into an electrolyte solution. For a 1D  $z:z$  electrolyte system, the potential  $\psi$  can be described by the Gouy-Chapman (GC) Equation:

$$\frac{\partial\psi}{\partial x} = -\sqrt{\frac{8k_B T c_0}{\epsilon_r \epsilon_0}} \sinh\left(\frac{ze\psi}{2k_B T}\right) \quad (8)$$

However, this model is sometimes too simple since it predicts that the concentration of the ions at the interface can infinitely increase with  $\psi$ . A better model for the double layer is known as the Gouy-Chapman-Stern (GCS) model, as shown in Figure 2.

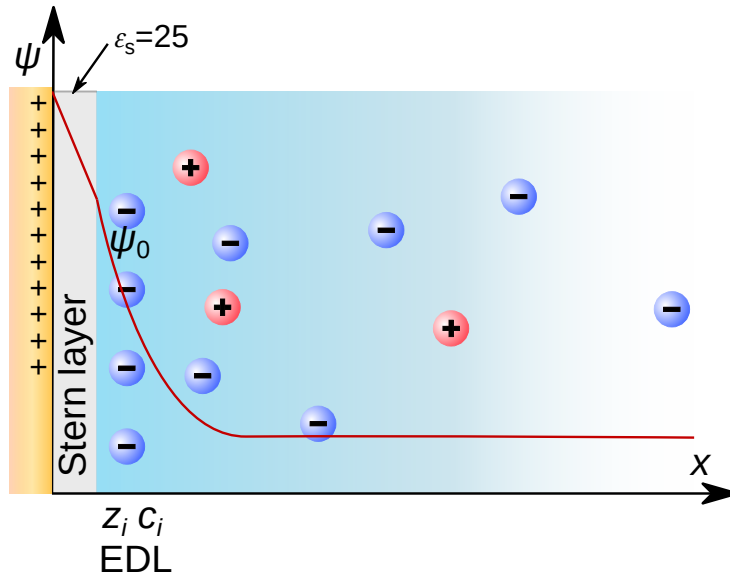


Figure 2: Scheme of the Gouy-Chapman-Stern model

In the GCS model, a region called the Stern layer exists between the conductor surface and the outer-most charges in the EDL. The Stern layer acts as a dielectric, so that no charges can move inside it. Outside the Stern layer, the charges can move freely and the Gouy-Chapman description is still valid. The thickness of the Stern layer is  $d_s$  and the dielectric constant is  $\epsilon_s$ . The dielectric constant of water is  $\epsilon_w$ .

1. In order to understand the limits of the Gouy-Chapman model, calculate the relative thickness  $d_{EDL}$  of the differential capacitance for the EDL using the GC model at  $\psi_0 = 1V$  for a 1 M KCl solution. Please explain your observation thoroughly.
2. What does the potential profile inside the Stern layer look like? Please also write down the boundary condition of  $\psi$  at the interface between Stern layer and EDL.
3. Assume  $d_s = 2.5 \text{ \AA}$ ,  $\epsilon_s = 25$ . When the potential on the conducting plate is fixed at  $\psi_0 = 500 \text{ mV}$ , compute the potential profiles for (i) 1 mM and (ii) 1 M KCl solutions at 300 K. Compare your results obtained from simple Gouy-Chapman equation and the GCS model.
4. Assume  $d_s = 2.5 \text{ \AA}$ ,  $\epsilon_s = 25$ . When the surface charge on the conducting plate is fixed at  $\sigma_M = 0.01 \text{ C/m}^2$ , compute the potential profiles for (i) 1 mM and (ii) 1 M KCl solutions

at 300 K. Compare your results obtained from simple Gouy-Chapman equation and the GCS model.

5. The differential capacitance of an electrode is defined as  $C_{\text{diff}} = \partial\sigma_M/\partial\psi_M$ , where  $\sigma_M$  and  $\psi_M$  are the charge density and potential on the electrode. Calculate the value of  $C_{\text{diff}}$  as a function of  $\psi_M$  for (i) 1 mM and (ii) 1 M KCl solutions. Compare the results obtained using simple Gouy-Chapman equation and the GCS model. The other parameters are the same as in Q3.4.
6. Now compare the results from Q3.5 for the GC and the GCS model by plotting the ratio of both differential capacitances, i.e.  $C_{\text{diff}}^{\text{GC}}/C_{\text{diff}}^{\text{GCS}}$ , as functions of potential  $\psi_0$  for both concentration separately. Try to find the regions (or points) in which both models coincide, if there is any.