NCCN
Nanomaterials: Catalysis, Colloids and Nanophotonics

Exam November 6, 2014

Choice (Advanced) Questions

You have to solve at least one of these parts

It is also allowed to do more than one part. Only the best result will be counted in your final grade.

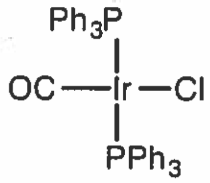
Please use a separate sheet of paper for every part

Don't forget to write down on each piece of paper:

- **your name and student #**
- **which part of the exam you solve**

Advanced exam questions Catalysis

(total 50 points)



A

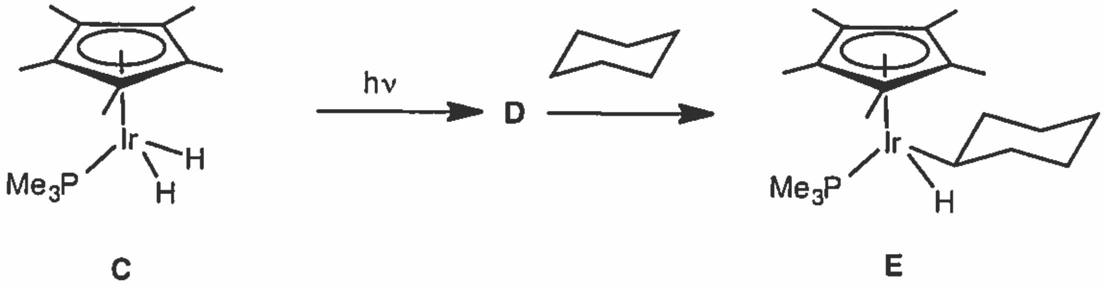
Like many transition metal complexes, compound **A** reacts with dihydrogen.

a) Draw the two main orbital interactions involved in the bonding and activation of H_2 to a molecular transition metal complex. (6p)

b) Draw the product of the reaction of **A** with H_2. Pay attention to the stereochemistry of the product and explain how it relates to the reaction mechanism. (6p)

c) Hydrogen reacts readily with many transition metal compounds, but methane and higher alkanes (C_nH_{2n+2}) are considerably less reactive and can often be used as inert solvents. Give two reasons explaining the difference in reactivity between H-H and C-H σ-bonds. (6p)

d) One way to generate reactive transition metal compounds able to activate alkanes is photochemical activation. Irradiating compound **C** in cyclohexane yields the cyclohexyl/hydride compound **E**. The reaction is postulated to proceed *via* an unobserved intermediate **D**. Propose a structure for **D** and assign its oxidation state, d-electron count, and number of valence electrons. (7p)



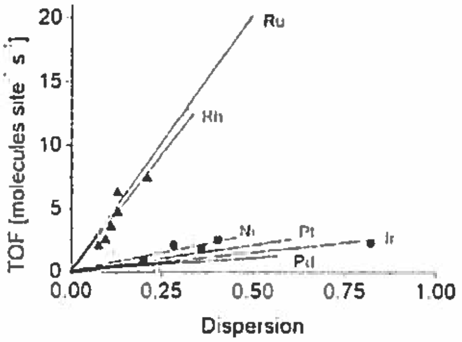
C **E**

The conversion of methane to syn gas by steam reforming over a heterogeneous catalyst is one of the most important industrial processes:

$$CH_4 + H_2O \longrightarrow CO + 3\ H_2$$

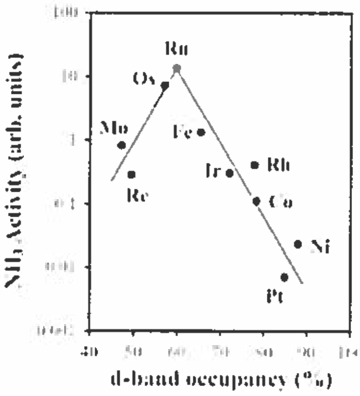
e) The graph below shows that catalytic activity of various metals increases with increasing dispersion (dispersion = number of surface atoms/total number of atoms). The table on the right lists some experimentally determined activation energies for methane activation over different metal surfaces. The metal surfaces are listed in order of decreasing surface coordination number (that is, Ru(0001) has the highest surface coordination number, a Pd atom the lowest).

1) Explain what the particle size dependence as shown in the graph tells you about the rate-determining step of the reaction. (6 p)
2) Why does the activation energy depend on the surface coordination number in the way shown in the table? (4 p)



	E_{act} (kJ/mol)
Ru(0001)	77
Ru(1120)	56
Rh(111)	67
Rh step	32
Pd (111)	66
Pd step	38
Pd atom	5

f) Ammonia synthesis ($N_2 + 3H_2 \rightarrow 2NH_3$) requires the dissociation of dinitrogen over a metal catalyst. Given is the activity of various supported metal catalysts for the synthesis of ammonia as a function of position in the periodic table (represented here as d-band occupancy). Explain in detail why such a volcano-type plot is observed. (7 p)



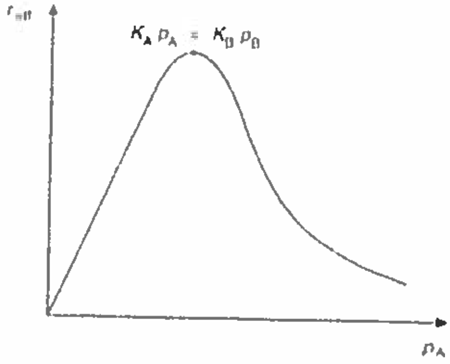
The elementary steps and the Langmuir-Hinshelwood expression for the rate of the reaction A + B → C are given below. A plot of the rate of the reaction as a function of the pressure of A is also given, at a constant value of the pressure of B; θ_X, the fraction of catalytic sites occupied by species X; N_T, the total amount of catalytic sites.

$A(g) + * \rightleftharpoons A^*$ fast/equilibrium K_a

$B(g) + * \rightleftharpoons B^*$ fast/equilibrium K_b

$A^* + B^* \xrightarrow{k_3} C^* + *$ rate-determining ste

$C^* \longrightarrow C(g) + *$ fast



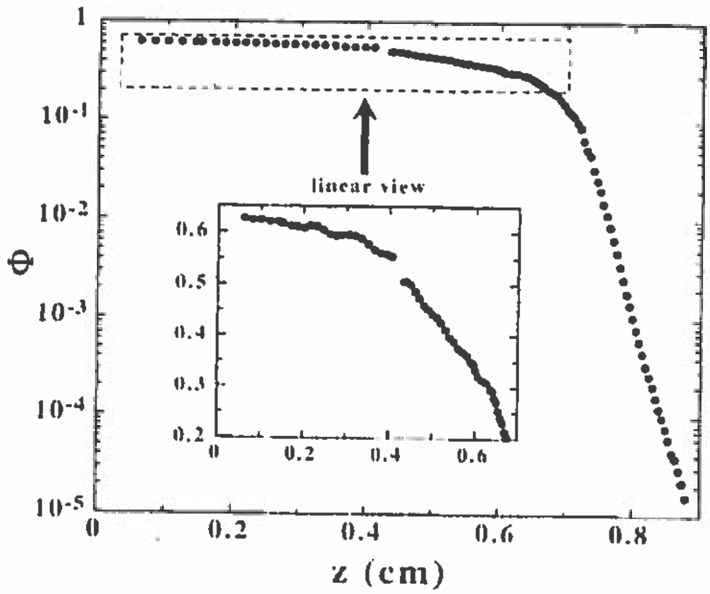
$$r = dp_C/dt = k_3\theta_A\theta_B$$

$$r = \frac{N_T . k_3 . K_A . K_B \cdot p_A \cdot p_B}{(1 + K_A \cdot p_A + K_B \cdot p_B)^2}$$

h) 1) Explain why the maximum rate is found at the specific value depicted in the graph. (4 p)
2) What are the orders in species A at high p_A and at low p_A? (4 p)

Colloids

Advanced questions



The graph shows the volume fraction Φ of monodisperse colloidal particles measured as a function of height z in a sedimentation-diffusion equilibrium (SDE) at room temperature. The particles have a radius of a = 90 nm and interact like *hard spheres*. The suspension medium was water, which has a density of 1.00 g/cm^3.

(a) Explain the general behavior of the data, in particular the jump at z = 0.42 cm and the exponential profile at low Φ. [20%]

(b) From the data, estimate the gravitational length and use it to calculate the density of the particles. [30%]

Suppose that you repeat the experiment, but this time in the presence of a uniform electric field applied horizontally across the tube.

(c) Estimate the order of magnitude of the electric field strength needed to observe a significant change in the position of the jump in volume fraction. Assume that the dielectric constant of the particles is 2.5 and of the solvent 78. [30%]

(d) At the electric field strength determined in the previous question sketch the new SDE. Discuss the main differences and similarities with the hard sphere case. [20%]

Boltzmann constant, k	1.38×10^{-23} J/K
Permittivity of vacuum, ε_0	8.85×10^{-12} CV^{-1}m^{-1}
Acceleration of gravity, g	9.8 m/s^2
Elementary charge unit, e	1.60×10^{-19} C
Avogadro's number, N_A	6.0×10^{23} mol^{-1}

$$f_{\text{sphere}} = 6\pi\eta a \qquad D = \frac{kT}{f} \qquad \langle r^2\rangle = 6Dt$$

$$\Phi(x) = \Phi(0)\exp\left(-\frac{x}{l_g}\right) \qquad l_g = \frac{kT}{\Delta mg} \qquad 2d\sin\theta = m\lambda$$

$$V(r) = \frac{Z^2e^2}{4\pi\varepsilon\varepsilon_0}\frac{e^{2\kappa a}}{(1+\kappa a)^2}\frac{e^{-\kappa r}}{r} - \frac{A_H}{12}\frac{a}{r-2a} \qquad \kappa = \left(\frac{\sum z_i^2 e^2 n_{0i}}{\varepsilon\varepsilon_0 k_B T}\right)^{\frac{1}{2}}$$

$$u_{\text{dip-dip}}(r) = \frac{p^2\left(1-3\cos^2\theta\right)}{4\pi\varepsilon_0\varepsilon_m r^3} \qquad \mathbf{p}_{\text{sphere}} = 4\pi\varepsilon_0\varepsilon_m a^3\frac{\varepsilon_p-\varepsilon_m}{\varepsilon_p+2\varepsilon_m}\mathbf{E}_0$$

Advanced exam questions Nanophotonics

a) Explain the difference between an anti-reflection coating and a randomized surface.

b) A scattering surface on top of a solar cell (thickness w) increases the light path length per scattering on average by <l>=2w when assuming a total reflecting back contact. Only $1/n_S^2$ (n_S = refractive index of semiconductor) of the rays (inside the cell) that strike the front surface again will leave the cell. Using

$$\sum_{i=0}^{\infty} i x^{i-1} = \frac{1}{(1-x)^2} \qquad (x < 1)$$

can you estimate the total path length enhancement expressed in n_S ?

c) For silicon this total increased path length can become as much as 50w. Using the Lambert Beer law with an absorption coefficient of $a = 10^4\ \mathrm{cm}^{-1}$, can you calculate how many of the original photons will reach this 50w? Use w=500 nm.

d) A solar cell has a short circuit current (J_{SC}) of 20 mA cm^{-2} and open circuit voltage of 0.50 V. By using texturing, the short circuit current is increased by 20%. Using the ideal diode equation:

$$J = J_{SC} + J_0\left(e^{qV/k_BT} - 1\right)$$

calculate the open circuit voltage which is expected with texturing.

k_B= 1.38 × 10^{-23} $\mathrm{m}^2\ \mathrm{kg}\ \mathrm{s}^{-2}\ \mathrm{K}^{-1}$

q= 1.60217657 × 10^{-19} coulombs

T=300 K

NCCN
Nanomaterials: Catalysis, Colloids and Nanophotonics

Exam November 6, 2014

Mandatory (Basic) Questions

You have to do all 3 parts

Please use a separate sheet of paper for every part

Don't forget to write down on each piece of paper:

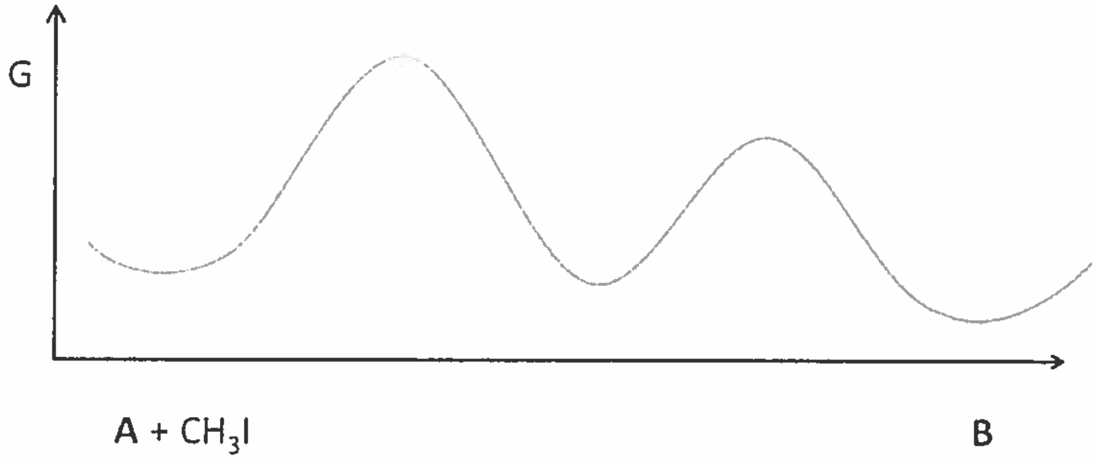
- **your name and student #**
- **which part of the exam you solve**

Basic exam questions Catalysis

(total 50 points)

The mechanism of the oxidative addition of CH_3I to iridium complex **A** to form compound **B** can be represented by the schematic reaction coordinate diagram depicted below. Please draw this diagram on the answer sheet to answer questions a) and b).

A **B**



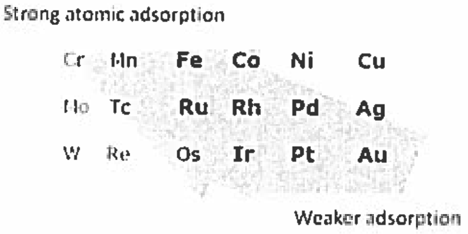
a) Indicate on this diagram the position of the intermediate(s) and transition state(s). How many elementary steps are there? (5p)

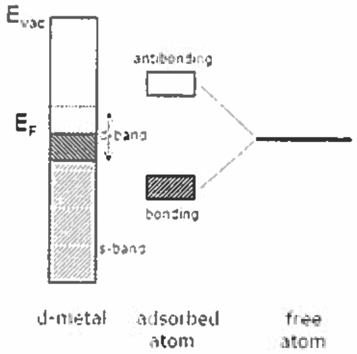
b) Indicate on the diagram the free enthalpy of reaction ($\Delta_r G$) and the free enthalpy of activation ($\Delta G^{\ddagger}$). (5p)

c) Suppose you need to measure the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation for this reaction using a linear fitting method. How do you proceed? (9p)

d) What are the number of valence electrons and the oxidation state of the iridium center in compounds **A** and **B** ? (6p)

e) The strength of atomic adsorption on a transition metal varies with the position of the metal in the periodic table and shows the following trend:





Given is also a simplified, schematic MO diagram for the adsorption of an atom on, e.g., Cr. Draw the equivalent MO diagram for a metal such as Rh and explain how this leads to a more weakly adsorbed atom. (6 pt)

f) Adsorption of a species on a surface is the first step in every reaction of heterogeneous catalysis. For an adsorbed species A in equilibrium with the gas phase, the surface coverage of A can be quantitatively described by the Langmuir isotherm:

$$A + * \underset{k_A^-}{\overset{k_A^+}{\rightleftharpoons}} A* \qquad \theta_A = \frac{K_A\, p_A}{1 + K_A\, p_A}$$

1) Describe the basic assumptions of the model when adsorption is described by Langmuir adsorption isotherms. (4 pt)
2) Show how the Langmuir adsorption isotherm as given above can be derived. (6 pt)

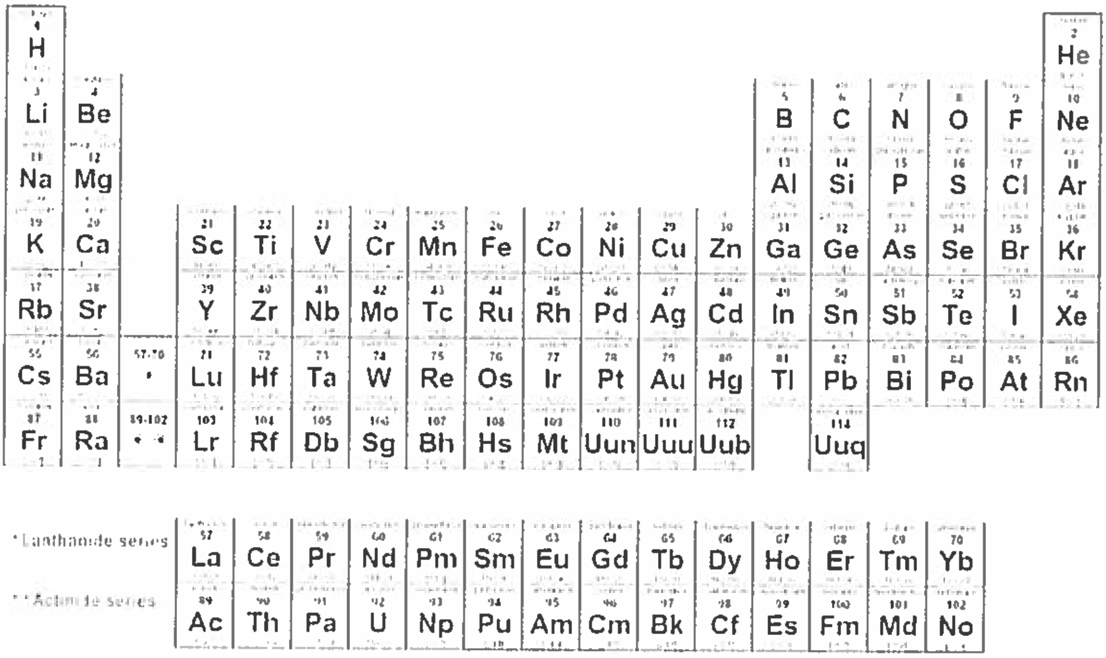
g) The oxidation of SO_2 on Pt catalysts proceeds in two steps:

a. $O_2 + 2* \rightarrow 2O*$
b. $SO_2 + O* \rightarrow SO_3 + *$

To give the overall reaction $2SO_2 + O_2 \rightarrow 2SO_3$

1) What mechanism is involved in this reaction? Explain what happens in the individual steps of the reaction. (5p)
2) Assuming that step a is rate-determining, how do you expect the turnover frequency (TOF) to depend on Pt particle size? (4p)

Annex I: Periodic Table



1 H																		2 He
3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-70 *	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-102 * *	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq				

*Lanthanide series	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
* *Actinide series	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Annex II: Thermodynamics and kinetics equations

For a generic reaction given as:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}$$

As a reminder, the equilibrium constant *K* is given by:

$$K = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$$

and can be related to the Gibbs free energy of reaction $\Delta_r G$

$$\Delta_r G = \Delta_r H - T\Delta_r S = -RT\ln(K)$$

Where $\Delta_r H$ and $\Delta_r S$ are the enthalpy and entropy of reaction, respectively.

The rate law relates the reaction velocity to the concentrations of the reactants:

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = k[\mathrm{A}]^n[\mathrm{B}]^m$$

Where k is the rate constant, n *and* m are order of the reaction in A and B, respectively. The overall reaction order is given by: $n+m$.

The temperature dependence of the rate constant is expressed by the Eyring equation:

$$k = \left(\frac{k_B T}{h}\right)\exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) = \left(\frac{k_B T}{h}\right)\exp\left(\frac{-\Delta H^{\ddagger} + T\Delta S^{\ddagger}}{RT}\right)$$

Where $\Delta G^{\ddagger}$ is the free enthalpy (or Gibbs free energy) of activation, $\Delta H^{\ddagger}$ the enthalpy of activation and $\Delta S^{\ddagger}$ the entropy of activation.

Physical constants:
Boltzmann constant: $k_B = 1.381 \bullet 10^{-23}\ \mathrm{m^2\ kg\ s^{-2}\ K^{-1}}$
Planck constant: $h = 6.626 \bullet 10^{-34}\ \mathrm{m^2\ kg\ s^{-1}}$
Gas constant: $R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$
Absolute zero: 0K = −273.15 °C

Basic questions on (magnetic) colloids – NCCN exam on November 6, 2014

Maghemite is a magnetic iron oxide with a bulk magnetization of 230 kA/m. A ferrofluid is made by dispersing maghemite nanoparticles in a liquid with negligible magnetic properties. 10.0 % of the volume of the ferrofluid consists of maghemite. The nanoparticles have a maghemite core with a single magnetic domain and a radius of 3.0 nm, surrounded by a shell of nonmagnetic polymer that brings the total radius up to 5.0 nm. The temperature is 300.0 K, solvent viscosity is 1.0×10^{-3} Pas, iron oxide density is 5.0 g/cm^3, solvent density if 0.9 g/cm^3, and the polymer shell is also 0.9 g/cm^3. Not all the information provided here is necessary to answer the questions.

(a) Make a schematic illustration of the magnetization of the ferrofluid as a function of the external magnetic field strength.

(b) Calculate the saturation magnetization of the ferrofluid.

(c) Calculate the magnetic dipole moment of a single nanoparticle.

(d) Calculate the dimensionless slope of the magnetization curve in the low-field limit.

(e) Calculate the magnetic interaction of two nanoparticles that touch each other in the head-to-tail configuration of the nanoparticle dipoles.

(f) Use your answer from (e) to argue whether the colloidal dispersion is likely to be stable (if your answer in (e) is wrong, your answer here will be considered correct if it draws the correct conclusion).

(g) Assuming that Néel relaxation is extremely rapid, explain how you expect the magnetization curve to change upon full evaporation of the liquid.

$$B=\mu_0 H(1+\chi) \qquad B=\mu_0(H+M) \qquad U=-\mu_0\vec{H}\cdot\vec{m}=-\mu_0 Hm\cos\theta \qquad V_{sphere}=\frac{4}{3}\pi a^3$$

$$L(\alpha)=\frac{e^{\alpha}+e^{-\alpha}}{e^{\alpha}-e^{-\alpha}}-\frac{1}{\alpha}=\coth(\alpha)-\frac{1}{\alpha} \qquad L(\alpha\to 0)=\alpha/3 \qquad \alpha=\mu_0 Hm/(k_B T) \qquad \omega=2\pi f$$

$$U_{\max}=-\frac{\mu_0 m^2}{2\pi(2a)^3} \qquad \tau_N=\tau_0\exp\left(\frac{KV}{k_B T}\right) \qquad \tau_B=\frac{3V\eta}{k_B T} \qquad \chi'=\chi_0\frac{\omega_c{}^2}{\omega_c{}^2+\omega^2} \qquad \chi''=\chi_0\frac{\omega_c\omega}{\omega_c{}^2+\omega^2}$$

$$P=\mu_0\pi\chi'' fH^2 \qquad F_{gravity}=V\Delta\rho g \qquad c(h)=c(0)\exp\left(-\frac{V\Delta\rho gh}{k_B T}\right) \qquad F_{viscous}=6\pi\eta av$$

$$F_{magnetic}=(\vec{m}\cdot\nabla)\vec{B} \qquad F_{magnetic,x}=\mu_0 m_x\frac{dH}{dx} \qquad P+\frac{\rho v^2}{2}+\rho gh-\mu_0\int_0^H MdH=C$$

Boltzmann constant, k_B	1.38×10^{-23} J/K	Elementary charge, e	1.6×10^{-19} C
Vacuum permeability, μ_0	$4\pi\times10^{-7}$ JA^{-2}m^{-1}	Number of Avogadro, N_A	6×10^{23} mol^{-1}
Acceleration of gravity, g	9.8 m/s^2	A/m per tesla	$10^7/(4\pi)$

Basic exam questions Nanophotonics

A light field with electric field E_0 shines on a silver particle with diameter 20 nm. The electrons on the particle will respond and form an electric dipole. The electric field of this dipole response is proportional to:

$$\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \frac{a^3}{r^3} E_0$$

With a = 20 nm (diameter), r = distance from particle center, ε_1 = dielectric constant of metal, ε_2 = dielectric constant of the surrounding medium.

a) What happens when $\varepsilon_1 \approx -2\varepsilon_2$?

b) For the silver particle ($\varepsilon_1 = -18$) at a distance of 10 nm from the surface we find a field enhancement of 5 times ($=5\times E_0$). What is the dielectric constant of the surrounding medium?

c) Since ε depends on the light wavelength, the maximum enhancement also does. How could we slightly shift the wavelength of the maximum enhancement of a silver particle?

d) When you enhance the electric field locally around a particle, the light field somewhere else becomes weaker. Knowing this, for what type of solar cells is the use of these silver particles interesting?

e) Without plasmonic particles a solar cell provides a current of 25 mA and a voltage of 0.8 V at maximum peak power. Using a plasmonic structure the efficiency of this solar cell is increased by 10%. The output voltage drops by 10 % with the plasmonic particles, what will the new current become?