<u>January 2008 RAE - Start time: 9:00 a.m., Monday, Jan. 14.</u>

There are three problems shown below, each on a separate page. Each student has to choose one and let Kathy Lopresti (lopresti@umd.edu) know by e-mail by **<u>1 p.m. today.</u>** You have until **<u>Wednesday, Jan. 23, at 12:00 noon,</u>** to complete and submit a written report. The written report should be e-mailed to Kathy Lopresti and a hard copy delivered to her by the due time.

The requirements for the written report, as explained on the ChBE website (http://www.chbe.umd.edu/grad/phd-aptitude.html) are:

The solution to the exam problem is to be in the form of a document not exceeding 10 double-space pages using a 12pt font. The 10 pages must include the title page, proposal body, and all figures; the number of pages used for references is unlimited.

The report **must** follow the following format:

1. It should include a single title page with a project summary.
2. It should include at most 5 pages dedicated to background information relevant to the particular RAE problem (including the figures of this section).
3. The remainder of the 10 page report must focus on proposed approach to solving the stated problem, any preliminary calculations or research results, the expected outcomes of the project, and a summary of the laboratory equipment and computational resources necessary to carry out the project.

The 10 page limit will be strictly enforced.

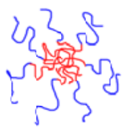
You are reminded that students are not allowed to consult with anyone during the RAE, including with faculty members. For procedural questions, you may contact members of the graduate committee (Drs. Adomaitis, Dimitrakopoulos, Raghavan, Zafiriou).

The oral exams will take place on **<u>Thursday, Jan. 24</u>**. Each student should plan on a brief (under 30 minutes) oral presentation. The presentation file can be brought to the examination room by the student on a memory stick. If this is not possible, please contact Kathy Lopresti prior to the examination time for alternate arrangements for transfering the file. A schedule with the exact times and room numbers for each student is given below. If unforeseen factors necessitate any changes, you will be informed by e-mail.

Arana Chavez, David; Time: 10:30 a.m. - 12:00 noon; Room: 2136
Breger, Joyce; Time: 1:30 p.m. - 3:00 p.m.; Room: 2118
Fuentevilla, Daphne; Time: 9:00 a.m. - 10:30 p.m.; Room: 2136
Gordon, Bradley; Time: 10:30 a.m. - 12:00 noon; Room: 2116
Kaplowitz, Daniel; Time: 3:00 p.m. - 4:30 p.m.; Room: 2136
Kim, Dongwhee; Time: 1:30 p.m. - 3:00 p.m.; Room: 2116
Luo, Yanting; Time: 3:00 p.m. - 4:30 p.m.; Room: 2116
Pendse, Pushkar; Time: 9:00 a.m. - 10:30 a.m.; Room: 2118
Rueger, Paul; Time: 1:30 p.m. - 3:00 p.m.; Room: 2136
Shahshahan, Negin; Time: 10:30 a.m. - 12:00 noon.; Room: 2118
Zhu, Yujie; Time: 9:00 a.m. - 10:30 a.m.; Room: 2116

Problem 1

Micelles form when one part of a molecule is attracted to the solvent and one part of the molecule is repelled by the solvent. These amphiphilic molecules can self-assemble into spherical aggregates with the solvophobic partss on the interiors (cores) of the aggregates and with the solvophilic parts on the exteriors (coronas) of the aggregates. Micelles can form from small molecule surfactants, from diblock copolymers A–B, (where **A is solvophobic** and **B is solvophilic**), or from triblock copolymers (A–B–A, B–A–B, or A-B-C, where C differs from A and B). The micellar structures are dynamic entities, nanometers in diameter, in chemical equilibrium with the free copolymers, and polydisperse in size and aggregation number (number of copolymers in the micelle).



Micelle formed from a A-B diblock copolymer with a solvophobic block A and a solvophilic block B.

You are interested in the production of gold nanospheres.

1) Present a method of synthesizing these nanospheres that uses micelles to control their size distributions. Discuss what you will vary in order to produce nanospheres of sizes ranging from 2 nm to 100 nm.

2) Discuss two methods of determining the size distributions of your nanospheres. What auxiliary information is required for these measurements and how will you obtain it?

3) Discuss at least two uses for your nanospheres. One use must involve the functionalization of the nanospheres. Explain the chemistry of this functionalization.

4) Discuss the technical issues in scaling your production up to a commercial level.

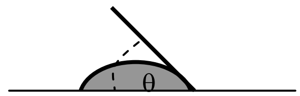
Suggested reference: Marie-Christine Daniel and Didier Astruc, Chem. Rev. 104, 293-346 (2004).

Problem 2

Consider a sessile drop of a liquid on a flat solid surface shown below in Figure 1. Typically, the relationship between equilibrium shape of the droplet and the interfacial tensions between the phases is given by the Young equation [1]

$$\gamma_{SL} + \gamma_{VL} \cos\theta = \gamma_{SV}$$

where θ is the contact angle (as shown in the schematic below), γSL is the interfacial tension between the solid and liquid phase, γVL is the interfacial tension between the vapor and liquid phase and γSV is the interfacial tension between the solid and vapor phase.



As noted by Gibbs, however, line tension also contributes to the equilibrium shape of the drop [2]. Line tension is defined in a continuum approach as excess free energy associated with the contact line at the three-phase boundary. The effect of line tension may be negligible in some cases, for example for larger droplets on a surface but line tension may contribute to interfacial phenomena particularly those involving interactions between small droplets and surfaces or between small solid particles and fluids, for example small (sub micron diameter) beads at an air-water interface, or at a water-oil interface [3, 4].

Review the two or three most common methods in the literature for measuring line tension. For a three-phase system consisting of glass, air and water, what would you expect for the magnitude of the line tension based upon what has been reported in the literature?

What are the main challenges associated with this type of measurement?

How would you experimentally determine the line tension for a three-phase system consisting of glass, air and water? What would be the greatest source of uncertainty in your measurement?

Discuss strategies to experimentally modify the glass surface so as to either reduce or increase the line tension.

[1] Israelachvili JN, 1992, *Intermolecular and Surface Forces*, (Academic Press)
[2] Gibbs JW, 1961, *The Scientific Papers of J. Willard Gibb*, vol. 1, (Ox Bow Press)
[3] Bresme F and Oettel M, 2007, “Nanoparticles at fluid interfaces”, Journal of Physics: Condensed Matter, vol. 19, 413101 (33pp)
[4] Guzzardi L and Rosso R, 2007, “Sessile droplets on a curved substrate: effects of line tension”, Journal of Physics A: Mathematical and Theoretical, vol. 40, 19-46.

Problem 3

The separation of molecular nitrogen and oxygen from air typically involves cryogenic distillation (CD). Although this traditional method is effective in separating these two components, it can be fairly expensive because it is highly energy intensive. For this RAE problem, take an example of a generic multi-step process used to make a desired product (**A**). This process releases a gas mixture of nitrogen and oxygen at a high temperature (1000 K). The process to make **A** requires several steps and molecular oxygen (95% purity) is used in an intermediate step. A new technology is desired to separate O_2 from N_2 at high temperatures and use it in the required intermediate step. For this problem, consider the following:

1) Review the current technologies used in separating N_2/O_2. This should include at least two methods that do not involve cryogenic distillation, but CD should be discussed. Clearly state the advantages and disadvantages of each technology.
2) Suggest a new technology to separate these gases that is effective at high temperature. The thermodynamics and mass transfer for gas separation should be discussed in detail. This new technology can be based on others discussed but must have something new and novel.
3) Discuss the design of experiments (wet lab, computational, or both) that will test this new technology. What experimental approaches will you use and why? Are there alternate approaches that can be used if your proposed experimental testing fails?