Chemistry 410B **Exam 3** **Spring 2008**

NAME:

Instructions:

1. Keep this exam closed until instructed to begin. Please write your name on this page but not on any other page.
2. Please silence any noisy electronic devices you have.
3. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam if you prefer.
4. To receive full credit for your work, please
   (a) show all your work, using the back of this sheet if necessary,
   (b) specify the correct units, if any, for your final answers,
   (c) stop writing and close your exam immediately when time is called.

Other notes:

- **Your best scores on 4 of the 5 questions will contribute to your grade.**
- Partial credit is usually available for all problems, so try each problem and do not erase any of your work.
- Each question is worth 25 points.

1. Consider a molecular dynamics simulation using a square well potential where

$$u_{\mathrm{sq}}(R) = \begin{cases} \infty & \text{if } R \leq R_1 \\ -\epsilon & \text{if } R_1 < R \leq R_2 \\ 0 & \text{if } R > R_2 \end{cases} .$$

To correct the motion of the particles, we need to calculate the force of any interaction between two molecules A and B.

(a) What is this force when A and B are separated by a distance $2R_2$?

(b) What is this force when A and B are separated by a distance $(R_1 + R_2)/2$?

(c) Use the change in potential energy to find an approximate expression for this force when the distance between A and B changes from $R_2 + (\Delta R/2)$ to $R_2 - (\Delta R/2)$, where $\Delta R \ll R_2 - R_1$.

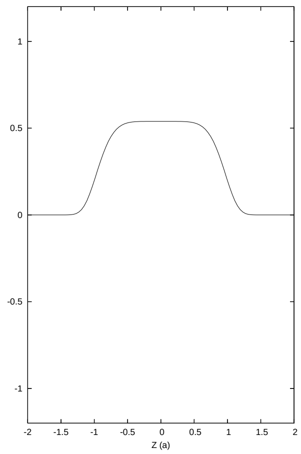
2. What will be the average speed (*not* relative speed) of $^{19}F_2$ molecules in a sample where the average collision energy is 15.0 kJ mol^{-1}?

3. If we flip a coin an even number of times N, there's a chance that we will get an equal number of heads and tails.

   (a) Find a general expression for this probability in terms of N.

   (b) Find the minimum number of flips so that this probability is less than 1/3.

4. A liquid is added to solvent with an initial (normalized) distribution at $t = 0$ of $\mathcal{P}(()Z) = Ae^{-(Z/a)^6}$, where $A = 0.53896$. This is a nearly constant value from $Z = 0$ to $Z = \pm a$, where it rapidly drops to zero. Find an expression for the flux as a function of Z, and sketch that function on the graph below.



5. Find the value of the absorption coefficient (including units) of a 0.100 M solution of pyrene that absorbs 12% of the radiation intensity when the pathlength is 1.00 cm.

Fundamental Constants

Avogadro's number	$\mathcal{N}_A$	$6.0221367 \cdot 10^{23}$ mol^{-1}
Bohr radius	$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	$5.29177249 \cdot 10^{-11}$ m
Boltzmann constant	k_B	$1.380658 \cdot 10^{-23}$ J K^{-1}
electron rest mass	m_e	$9.1093897 \cdot 10^{-31}$ kg
fundamental charge	e	$1.6021773 \cdot 10^{-19}$ C
permittivity factor	$4\pi\epsilon_0$	$1.113 \cdot 10^{-10}$ C^2 J^{-1} m^{-1}
gas constant	R	8.314510 J K^{-1} mol^{-1}
	R	0.08314510 L bar K^{-1} mol^{-1}
	R	0.08206 L atm K^{-1} mol^{-1}
hartree	$E_\mathrm{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ J
Planck's constant	h	$6.6260755 \cdot 10^{-34}$ J s
	$\hbar$	$1.05457266 \cdot 10^{-34}$ J s
proton rest mass	m_p	$1.6726231 \cdot 10^{-27}$ kg
neutron rest mass	m_n	$1.6749286 \cdot 10^{-27}$ kg
speed of light	c	$2.99792458 \cdot 10^{8}$ m s^{-1}

Unit Conversions

	K	cm^{-1}	kJ mol^{-1}	kcal mol^{-1}	erg	kJ
kHz =	$4.799 \cdot 10^{-8}$	$3.336 \cdot 10^{-8}$	$3.990 \cdot 10^{-10}$	$9.537 \cdot 10^{-11}$	$6.626 \cdot 10^{-24}$	$6.626 \cdot 10^{-34}$
MHz =	$4.799 \cdot 10^{-5}$	$3.336 \cdot 10^{-5}$	$3.990 \cdot 10^{-7}$	$9.537 \cdot 10^{-8}$	$6.626 \cdot 10^{-21}$	$6.626 \cdot 10^{-31}$
GHz =	$4.799 \cdot 10^{-2}$	$3.336 \cdot 10^{-2}$	$3.990 \cdot 10^{-4}$	$9.537 \cdot 10^{-5}$	$6.626 \cdot 10^{-18}$	$6.626 \cdot 10^{-28}$
K =	1	0.6950	$8.314 \cdot 10^{-3}$	$1.987 \cdot 10^{-3}$	$1.381 \cdot 10^{-16}$	$1.381 \cdot 10^{-26}$
cm^{-1} =	1.4388	1	$1.196 \cdot 10^{-2}$	$2.859 \cdot 10^{-3}$	$1.986 \cdot 10^{-16}$	$1.986 \cdot 10^{-26}$
kJ mol^{-1} =	$1.203 \cdot 10^{2}$	83.59	1	0.2390	$1.661 \cdot 10^{-14}$	$1.661 \cdot 10^{-24}$
kcal mol^{-1} =	$5.032 \cdot 10^{2}$	$3.498 \cdot 10^{2}$	4.184	1	$6.948 \cdot 10^{-14}$	$6.948 \cdot 10^{-24}$
eV =	$1.160 \cdot 10^{4}$	$8.066 \cdot 10^{3}$	96.49	23.06	$1.602 \cdot 10^{-12}$	$1.602 \cdot 10^{-22}$
hartree =	$3.158 \cdot 10^{5}$	$2.195 \cdot 10^{5}$	$2.625 \cdot 10^{3}$	$6.275 \cdot 10^{2}$	$4.360 \cdot 10^{-11}$	$4.360 \cdot 10^{-21}$
erg =	$7.243 \cdot 10^{15}$	$5.034 \cdot 10^{15}$	$6.022 \cdot 10^{13}$	$1.439 \cdot 10^{13}$	1	10^{-10}
J =	$7.243 \cdot 10^{22}$	$5.034 \cdot 10^{22}$	$6.022 \cdot 10^{20}$	$1.439 \cdot 10^{20}$	10^{7}	10^{-3}
dm^3 bar =	$7.243 \cdot 10^{24}$	$5.034 \cdot 10^{24}$	$6.022 \cdot 10^{22}$	$1.439 \cdot 10^{22}$	$1.000 \cdot 10^{9}$	0.1000
kJ =	$7.243 \cdot 10^{25}$	$5.034 \cdot 10^{25}$	$6.022 \cdot 10^{23}$	$1.439 \cdot 10^{23}$	10^{10}	1

distance	1 Å =	10^{-10} m	
mass	1 amu =	$1.66054 \cdot 10^{-27}$ kg	
energy	1 J =	1 kg m^2 s^{-2}	= 10^7 erg
force	1 N =	1 kg m s^{-2}	= 10^5 dyn
electrostatic charge	1 C =	1 A s	= $2.9979 \cdot 10^9$ esu
	1 D =	$3.3357 \cdot 10^{-30}$ C m	= $1 \cdot 10^{-18}$ esu cm
magnetic field strength	1 T =	1 kg s^{-2} A^{-1}	= 10^4 gauss
pressure	1 Pa =	1 N m^{-2}	= 1 kg m^{-1} s^{-2}
	1 bar =	10^5 Pa	= 0.98692 atm

Some equations

Einstein equation
$$C_{Vm} = \frac{3N_A\omega_E^2 e^{\omega_E/(k_BT)}}{k_BT^2(e^{\omega_E/(k_BT)}-1)^2}$$

Debye theory
$$C_{Vm} = \frac{9N_Ak_B^4T^3}{\omega_D^3}\int_0^{\omega_D/(k_BT)}\frac{x^4e^xdx}{(e^x-1)^2}$$

blackbody
$$\rho(\nu)d\nu = \frac{8\pi h\nu^3 d\nu}{c^3(e^{h\nu/(k_BT)}-1)}$$

speeds
$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}}$$
$$v_{\rm rms} = \sqrt{\frac{3k_BT}{m}}$$
$$v_P = \sqrt{\frac{2k_BT}{m}}$$
$$\langle v_{AA}\rangle = 4\sqrt{\frac{k_BT}{\pi m}}$$

collisions
$$\langle E_{\rm AB}\rangle = \frac{3k_BT}{2}$$
$$\gamma = \rho\sigma\langle v_{AA}\rangle$$
$$\lambda = \frac{1}{\rho\sigma}$$

random walk
$$\mathcal{P}(k) = \frac{N!}{2^N\frac{N+k}{2}!\frac{N-k}{2}!}$$

diffusion
$$\mathcal{P}(x) = \frac{1}{\sqrt{2\pi}s}e^{-x^2/(2s^2)}$$
$$\mathcal{P}(r) = \frac{4\pi}{\sqrt{8\pi^3}s^3}e^{-r^2/(2s^2)}r^2$$
$$\mathcal{P}(r,t) = \frac{\pi}{2(\pi Dt)^{3/2}}e^{-r^2/(4Dt)}r^2$$
$$D \approx \frac{\lambda^2\gamma}{2} = \frac{\langle v_{\rm AA}\rangle}{2\rho\sigma}$$

Fick's laws
$$J(x_0) = -D\left(\frac{d\rho}{dx}\right)|_{x_0}$$
$$\frac{d\rho}{dt} = D\frac{d^2\rho}{dx^2}$$

Beer's laws
$$\log_{10}\frac{I}{I_0} = -\epsilon cl$$