Chemistry 40642/60642   Spring 2016
Professor J. Daniel Gezelter   Due Friday 4/22/2016

<center>Problem Set 4</center>

Choose either the Lennard-Jones fluid problem or the Langevin double-well problem. If you work in a liquid simulation group (i.e. Maginn, Gezelter, Corcelli, Whitmer) you *must* choose the Langevin problem. *It is dangerous to go alone!* You are strongly encouraged to work in groups of 2-3 students. START EARLY and come talk to me to help get past any difficulties.

1. To do this problem, you will need to procure or write your own Lennard-Jones molecular dynamics program for simulating a simple fluid. You will use this program to generate a time series of configurations of the liquid. From this set of saved configurations, you will compute the pair distribution function, $g(r)$, and the velocity autocorrelation function, $\langle v(t)v(0)\rangle$, for a number of different temperatures and densities.

    (a) The direct correlation function, $c(r)$ represents the direct correlation between two particles in a system containing $N-2$ other particles. This direct correlation function can be expressed as:
    $$c(r) = g(r) - g_{indirect}(r)$$
    where $g(r)$ is the standard radial distribution function.

    We can postulate the existence of a potential of mean force $w(r)$ for a simple liquid that approximates the interactions with all of the other atoms in the liquid:
    $$g(r) = e^{-\beta w(r)}$$

    and the differences between the potential of mean force and the pair potential, $v(r)$ result in the *indirect* contributions to the liquid's structure:
    $$g_{indirect}(r) = e^{-\beta[w(r)-v(r)]}$$

    It is also convenient to introduce one last function,
    $$y(r) = e^{\beta v(r)}g(r)$$

    a) Prove analytically that $c(r) = f(r)y(r)$. What is $f(r)$?

    b) Plot all of the functions mentioned above for the Lennard-Jones fluid at the following (T^*, ρ^*) points: (1.5, 0.85) (1.5, 0.94), (1.3, 1.0)

    c) Under which conditions would it be reasonable to approximate the potential of mean force by the pair potential?

    d) If we approximate the potential of mean force by the pair potential what is the relationship between the direct correlation function and $g(r)$?

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(b) Plot the normalized velocity autocorrelation function, $\langle v(t)v(0)\rangle/\langle v^2\rangle$ for each of those same state points: $(T^*, \rho^*) = (1.5, 0.85)$, $(1.5, 0.94)$, and $(1.3, 1.0)$. You will almost certainly need to write a program to do this calculation.

(c) Compute the Fourier transform of the symmetrized velocity autocorrelation functions to find the power spectrum for the Lennard-Jones fluid in these conditions.

2. Consider the following double-well potential model for chemical reactions,

$$V(x) = \frac{1}{4}bx^4 - \frac{1}{2}ax^2 \tag{1}$$

where a and b are positive constants.

(a) In the reactant well, we can approximate the potential as:

$$V_r(x) \approx V_r(x_0) + \frac{1}{2}m\omega_0^2(x - x_0)^2. \tag{2}$$

Find x_0 and ω_0 for the potential given in Eq. (1). m is the mass of the particle that is crossing the barrier.

(b) In classical transition state theory, the rate of reaction is given by

$$k^{TST} = \frac{\omega_0}{2\pi}e^{-\beta\Delta V_{cl}} \tag{3}$$

where ΔV_{cl} is the difference in energy between the bottom of the reactant well and the top of the barrier. Find an analytic expression for the k^{TST} for the potential in Eq. (1) in terms of a, b, m, and T.

(c) Write a program which performs a Langevin simulation on a particle that starts at the transition state ($x = 0$) with an initial velocity ($\dot{x}(0)$) chosen randomly from a Maxwell-Boltzmann distribution. Use the absolute value function to insure that the particle is moving towards the reactant ($x > 0$) side when the simulation starts. Remember that the Langevin equation with static friction is

$$m\ddot{x} = -\frac{\partial V}{\partial x} - \xi\dot{x}(t) + R(t) \tag{4}$$

and the second fluctuation dissipation theorem tells us that $\xi = \beta\langle R^2\rangle$. That is, for a given friction and temperature, we also know the second moment for the distribution of the gaussian random force.

(d) The classical rate can be obtained from the reactive flux time correlation function,

$$k_{cl} = \frac{1}{x_R}\langle\dot{x}(0)\delta[x^* - x(0)]h_p[x(t_{plateau})]\rangle \tag{5}$$

Your simulation program takes care of the delta function by starting the trajectories from the transition state ($x(0) = 0$), and takes care of the thermal average by using

a Maxwell-Boltzmann distribution of initial velocities $(\dot{x}(0)$. To compute the reactive flux correlation function, you just need to accumulate *velocity-weighted* statistics on the fraction of trajectories that are on the product side $(x > 0)$ in a particular time t. This weighted fraction will eventually stabilize or plateau, and the classical rate constant is the value this correlation function reaches after the plateau time. (x_R is the equilibrium mole fraction of the reactant.)

(e) Transition state theory is not an exact theory, so the classical rate is often related to the TST rate by a scaling factor,

$$k_{cl} = \kappa k^{TST} \tag{6}$$

Plot κ as a function of solvent friction. Can you explain the behavior at low values of ξ? What's going on with the high values of ξ?