

Chemistry 276 - Spring 2009-10 - Advanced Physical Chemistry

Problem Set (due 10/27/09 in class)

1 A simple model for self-diffusion

Consider the following model for calculating the self-diffusion coefficient of a molecule in a gas phase. The quantity to calculate first is, of course, the velocity autocorrelation function. Then calculate the area under the function to get the diffusion constant.

Suppose the velocity of each molecule initially has a Maxwell-Boltzmann distribution. Each molecule is subject to collisions by other molecules in the gas. Regard these collisions as instantaneous. Also, for the sake of simplicity, assume that the velocity of a molecule after a collision also has a Maxwell-Boltzmann distribution and is statistically independent the velocity before the collision.¹

Let the collision frequency of the molecule be ν . That is, νdt is equal to the probability that the molecule will suffer a collision in any infinitesimal time interval of length dt . Assume that ν is a constant, independent of the velocity of the molecule.²

1. Obtain a simple expression for the velocity autocorrelation function $\langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle$ for this model, where \mathbf{v}_i is the velocity of molecule i .
2. From your result for the velocity autocorrelation function, obtain a simple expression for the self-diffusion coefficient.
3. Let σ be the approximate diameter of the molecule and of the other molecules in the gas. Let n be the number density of the other molecules

¹This is a strong assumption, but it is not all that unreasonable. The momentum of the molecule after the collision is affected by its momentum before the collision, but lots of other things affect it as well, including the momentum of the thing it collides with as well as the details of how the two molecules approach one another (head-on collision, glancing collision, etc.) It is in general a better approximation when the molecule is lighter than the other molecules in the gas, and it can be a very bad approximation when it is much heavier than the other molecules.

²This is an approximation that obscures the details of the true collision process but that does not give physically unreasonable results.

in the gas. Estimate ν in terms of σ and n . (Hint: use the type of reasoning you might have learned in undergraduate physical chemistry courses when you discussed kinetic theory of gases.)

4. Express the velocity autocorrelation function and the self-diffusion coefficient in terms of σ and n .

2 Linear response theory calculation of chemical reaction rate constants

In the discussion in class, I compared the macroscopic theory of first order chemical kinetics with a microscopic description of a system consisting of one reacting molecule in solution. Does this mean that the calculation was wrong?

In fact the answer we got in class was correct as long as the reacting molecules are present in such low concentration that they do not affect one another in any way. Let's assume then that the concentration of reacting molecules is very small. (The concentration of solvent need not be small, however.)

At a crucial point in the discussion, we obtained the following result:

$$k = k_f + k_r = -\frac{\dot{C}_{\delta n_A \delta n_A}(\Delta t)}{C_{\delta n_A \delta n_A}(0)} \quad (1)$$

We proceeded as if the functions on the right here were those for a system containing a single reacting molecule.

To do it 'right', we should have considered these functions for a system containing a macroscopic number of solutes.

Suppose our system contains N solutes. Then the appropriate dynamical variable is

$$n_A(\Gamma) = \sum_{i=1}^N n_{Ai}(\Gamma) = \sum_{i=1}^N \Theta(-q_i)$$

where $n_A(\Gamma)$ is the number of A molecules in the system when the system is at point Γ in phase space, $n_{Ai}(\Gamma)$ is one if molecule i is in the A form and 0 if it is in the B form, and q_i is the reaction coordinate of molecule i . We

used the fact that $n_{A_i}(\Gamma) = \Theta(-q_i)$, where it is understood that the q_i on the right of these equations is the reaction coordinate for molecule i when the system is in state Γ .

Make the following assumptions:

- The properties of different molecules at all times are statistically independent.
- In particular this implies that $n_{A_i}(\Gamma, t)$ is statistically independent of $n_{A_j}(\Gamma, t')$ if $i \neq j$ for all values of t and t' .

Using these assumptions, evaluate the right side of Eq. (1) the ‘right’ way, i.e. taking into account that there are many reacting molecules in the system. See what difference it makes to the derivation.

3 An important feature of the dynamics of a classical mechanical system subject to a time dependent external field

Consider a classical system whose coordinates and momenta are Q^N, P^N .

1. Suppose the system has a time independent Hamiltonian $H_0(Q^N, P^N)$. Consider the value of H_0 as a function of time for a specific system. This could be denoted by $H_0(Q^N(t), P^N(t))$, where the $Q^N(t), P^N(t)$ satisfy Hamilton’s equations.

Show that the time derivative of this quantity is zero. (The physical meaning of this result is that the energy of an isolated system is conserved.)

2. Suppose the system has a time dependent Hamiltonian

$$H(Q^N, P^N, t) = H_0(Q^N, P^N) - g(t)B(Q^N, P^N)$$

Consider the value of H as a function of time for a specific system. This could be denoted $H(Q^N(t), P^N(t), t)$, where the $Q^N(t), P^N(t)$ satisfy Hamilton’s equations of motion (with the new time-dependent Hamiltonian, of course).

Show that the time derivative of this quantity is equal to

$$-\dot{g}(t)B(Q^N(t), P^N(t))$$

In other words, at each instant of time, the following holds.

$$\frac{d}{dt}H_0(Q^N(t), P^N(t)) - g(t)\frac{d}{dt}B(Q^N(t), P^N(t)) = 0$$

4 Linear response theory with multiple fields

Consider a classical system of the type in the previous problem that is subject to several fields. The time dependent Hamiltonian is of the form

$$H(Q^N, P^N, t) = H_0(Q^N, P^N) - \sum_{i=1}^n g_i(t)B_i(Q^N, P^N)$$

The various fields have their own time dependent amplitudes $g_i(t)$ and each couples to a different dynamical variable of the system $B_i(Q^N, P^N)$. The system would be in equilibrium in the absence of the applied fields, and we are interested in the linear response of the system to the applied fields. (We have discussed in class the situation in which there is only one applied field. That discussion in effect led to definitions of $\chi_{B_j B_i}(t)$ for all choices of B_i and B_j , including the case of $B_i = B_j$. You should use these functions in answering the following questions.)

1. What is the most general form for the linear response of $\langle B_j(t) \rangle_{ne}$ to the set of applied fields $g_i(t)$ for $i = 1 \dots n$?
2. Suppose each field is oscillatory with the same frequency.

$$g_i(t) = g_{i0} \cos(\omega t + \phi_i)$$

(Different fields can have different amplitudes g_{i0} and different phases ϕ_i , however.) Calculate the rate at which the system absorbs energy from the set of applied fields by averaging the energy absorption rate over one period of the oscillations.

3. Show, using very general assumptions about the correlation functions of the B_i , that the rate of energy absorption must be positive for all choices of the phases and amplitudes of the individual fields.