Advanced Transport Phenomena II
ChE 548
Department of Chemical Engineering
University of Tennessee, Knoxville
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Midterm Examination
Administered: March 1, 2002

Problem 1.
For a gas at low density, we can use the mean free path arguments of kinetic theory to obtain an estimate of the self-diffusivity,

$$D_{self,A} = \frac{2}{3}\sqrt{\frac{kT}{\pi m_A}}\frac{1}{\pi \sigma_A^2}\frac{1}{n} \qquad \text{(BSL 17.3-9)}$$

In problem 2 of homework 2, you used MD simulations to examine the temperature and density dependence of the self-diffusivity of a low density gas. (See the Table below and attached plots of your work.)

$k = 1.38066\text{x}10^{-23}$ J/K/molecule
$N_{av} = 6.02205\text{x}10^{23}$ molecules/mole
1 amu (atomic mass unit) = $1.66056\text{x}10^{-27}$ kg

Self Diffusion Coefficient for Acetylene at at T = 300K and n = $2.4583\text{x}10^{-5}$ molecules/Å^3	
Team 1	$0.73\text{x}10^{-5}$ m^2/s
Team 2	$1.33\text{x}10^{-5}$ m^2/s

(a) Consider your self-diffusivity for acetylene (m_A = 26.04 amu, σ_A = 4.114 Å) at T = 300K and n = $2.4583\text{x}10^{-5}$ molecules/Å^3. What is the error between the prediction of kinetic theory and your result? Please report the error as a percent of your simulation result.

$$D_{self,A} = \frac{2}{3}\sqrt{\frac{1.38066\cdot 10^{-23}(300)}{\pi\left(26.04\cdot 1.66056\cdot 10^{-27}\right)}}\frac{1}{\pi\left(4.114\cdot 10^{-10}\right)^2}\frac{1}{\left(2.4583\cdot 10^{-5}\cdot 10^{30}\right)}$$

$$D_{self,A} = 0.8906\cdot 10^{-5}\frac{m^2}{s}$$

$$error_{team1} = 100 * \frac{\left|D_{theory} - D_{sim}\right|}{D_{sim}} = 22\%$$

$$error_{team2} = 100 * \frac{\left|D_{theory} - D_{sim}\right|}{D_{sim}} = 33\%$$

(b) Do your simulations confirm or contradict the temperature and density dependence of the self-diffusion coefficient from kinetic theory? Discuss your reasoning.

The plots of both teams appear to show a hyperbolic (1/x) relationship between self-diffusivity and density. This is predicted by kinetic theory.

The plots of both teams showed a gradual, monotonic increase in diffusivity with temperature. It could certainly be a square root dependence, as predicted by kinetic theory, but it is difficult to tell exactly without doing a more quantitative analysis.

(c) Using kinetic theory *and* your simulation result for acetylene, please report the self-diffusivity for methane (m_A = 16 amu, σ_A = 3.822 Å) at T = 300K and n = 2.4583x10^{-5} molecules/Å^3.

Here we will use a corresponding states argument. We divide equation (BSL 17.3-9) by itself.

$$\frac{D_{self,A}}{D_{self,B}} = \frac{\frac{2}{3}\sqrt{\frac{kT}{\pi m_A}}\frac{1}{\pi \sigma_A^2}\frac{1}{n}}{\frac{2}{3}\sqrt{\frac{kT}{\pi m_B}}\frac{1}{\pi \sigma_B^2}\frac{1}{n}} = \frac{\sigma_B^2}{\sigma_A^2}\sqrt{\frac{m_B}{m_A}}$$

$$D_{self,A} = \frac{\sigma_B^2}{\sigma_A^2}\sqrt{\frac{m_B}{m_A}}D_{self,B}$$

Let A= Methane and let B = acetylene.

$$D_{self,A} = \frac{(4.114)^2}{(3.822)^2}\sqrt{\frac{26.04}{16}}0.73 \cdot 10^{-5} = 1.079 \cdot 10^{-5}\frac{m^2}{s}$$ for team 1

$$D_{self,A} = \frac{(4.114)^2}{(3.822)^2}\sqrt{\frac{26.04}{16}}1.33 \cdot 10^{-5} = 1.966 \cdot 10^{-5}\frac{m^2}{s}$$ for team 2

Problem 2.

You show your microcanonical ensemble MD simulation results to a colleague. He looks at your averge value of the potential energy and the standard deviation of the potential energy (which is equal to the standard deviation of the kinetic energy). He argues that you need to run your simulations for a longer time because your standard deviation of the potential energy is too large relative to the average value. You have already performed a sensitivity analysis on the number of time steps and determined that the average potential energy was not a function of simulation duration. Does your colleague have a legitimate point? If so, why? If not, how do you explain to your colleague that he is wrong?

Solution:

The colleague does not have a legitimate point. The fluctuations of the potential energy and of other thermodynamic variables are not fluctuations due to "noise in the data". As such, these fluctuations can not be reduced by reducing the statistical error of the simulation by such methods as increasing the number of molecules in the simulation or increasing the duration of the simulation.

These fluctuations are fixed by thermodynamics. If you recall from the lecture notes, the heat capacity is related to the standard deviation of the potential energy via the relation:

$$\sigma_U^2 = \frac{3}{2} N k_b^2 T^2 \left(1 - \frac{3}{2} \frac{N k_b}{C_v} \right) \tag{28}$$

Thus the standard deviation of the potential energy is used to define the heat capacity. Following the erroneous logic of your colleague, you could run the simulations for larger systems and longer times and the standard deviation should approach zero. Well, if the standard deviation approached zero, then the heat capacity would approach $\frac{3}{2} N k_b$, which is the value for a monatomic gas in the ideal gas limit. Of course, since we are not simulating an ideal gas, it makes no sense for the heat capacity to approach that limit.

If you really wanted a standard deviation on the potential energy from one simulation to another, you would have to run several simulations, compute average values of the potential energy from each one. Then, you could compute a sample standard deviation from those average values.