Exam 1
ChE 548
Spring, 2007

Problem 1.

Based on the results of Homework 3, answer the following questions.
(a) In an MD simulation, does it take longer for a gas or liquid phase to reach the Einstein infinite time limit in order to get a good diffusivity?
(b) Based on your reasoning in (a), will it take longer for a simulation to reach the Einstein infinite time limit at low or high temperature?
(c) In a binary mixture, which component will have the higher self-diffusivity, the one with the higher or lower molecular weight? Why?
(d) In a binary mixture, which component will have the higher Fickian diffusivity, the one with the higher or lower molecular weight? Why?
(e) What’s the general rule for the minimum number of molecules in an MD simulation?

Problem 1 solution.

(a) In an MD simulation, does it take longer for a gas or liquid phase to reach the Einstein infinite time limit in order to get a good diffusivity?

It takes longer for the gas to reach the long-time limit, because diffusion is dependent on the Brownian motion induced by collisions and collisions are less frequent in dilute systems.

(b) Based on your reasoning in (a), will it take longer for a simulation to reach the Einstein infinite time limit at low or high temperature?

Increasing the temperature, increase the mean molecular velocity, which increases the frequency of collisions. Thus the low temperature simulation will take longer to reach the long-time limit.

(c) In a binary mixture, which component will have the higher self-diffusivity, the one with the higher or lower molecular weight? Why?

At a given temperature, the mean velocity of a molecule is inversely proportional to the square root of the molecular weight. Thus light molecules move faster than heavy molecules. As a result, light molecules have a high self-diffusivity.

(d) In a binary mixture, which component will have the higher Fickian diffusivity, the one with the higher or lower molecular weight? Why?

Trick question. In a binary mixture, there is only one independent Fickian diffusivity and if you choose your frame of reference right it is the same for both components, regardless of molecular weight.

(e) What’s the general rule for the minimum number of molecules in an MD simulation?

There are two rules for minimum numbers. You must choose the larger of these two minima. First, you need enough molecules to get good statistics. For low density systems like gases, this rule dominates. Clearly, you never want to simulate with less than 100 molecules. Sometimes, you need much more than that if the quantity that you are interested in has statistical problems associated with it. Second, every dimension of a simulation volume must be larger than twice the neighbor distance. Specifically, for a cubic simulation volume

$$\ell_{\min} = 2r_{nbr}$$

$$V_{\min} = \ell_{\min}^3 = 8r_{nbr}^3$$

$$N_{\min} = \rho V_{\min} = \rho\ell_{\min}^3 = 8\rho r_{nbr}^3$$

This allows the molecule to see itself as in the middle of an infinite system. This rule generally dominates for dense phases.

Problem 2.

The corresponding states charts for shear viscosity, thermal conductivity and self-diffusivity appear on pages 22, 272 and 522 respectively of BSL2.

(a) Report the trends in shear viscosity, thermal conductivity and self-diffusivity as a function of temperature for the *ideal gas* based on the corresponding states chart, e.g. do these properties increase or decrease with temperature?
(b) Equation (1.4-8) on page 24, (9.3-11) on page 275 and (17.3-8) on page 526 provide estimates from kinetic theory on the temperature dependence of the shear viscosity, thermal conductivity and self-diffusivity as a function of temperature for the ideal gas. Do these equations provide the same temperature trends as the corresponding states chart in part (a)?
(c) Are all trends with respect to temperature the same for shear viscosity, thermal conductivity and self-diffusivity of the *ideal gas*?
(d) What is the molecular basis for the trends observed in part (a)?

(e) Report the trends in shear viscosity, thermal conductivity and self-diffusivity as a function of temperature for the *liquid* based on the corresponding states chart, e.g. do these properties increase or decrease with temperature?
(f) Equation (1.5-11) on page 31, (9.4-3) on page 279 and (17.4-5) on page 529 provide estimates from a mixture of theory and empiricism on the temperature dependence of the shear viscosity, thermal conductivity and self-diffusivity as a function of temperature for the *liquid*. Do these equations provide the same temperature trends as the corresponding states chart in part (e)?
(g) Are all trends with respect to temperature the same for shear viscosity, thermal conductivity and self-diffusivity of the *liquid*?
(h) What is the molecular basis for the trends observed in part (e)?

Problem 2 Solution:

(a) Report the trends in shear viscosity, thermal conductivity and self-diffusivity as a function of temperature for the *ideal gas* based on the corresponding states chart, e.g. do these properties increase or decrease with temperature?

Based on the corresponding states chart, for the ideal gas, the shear viscosity, thermal conductivity and self-diffusivity increase with temperature.

(b) Equation (1.4-8) on page 24, (9.3-11) on page 275 and (17.3-8) on page 526 provide estimates from kinetic theory on the temperature dependence of the shear viscosity, thermal conductivity and self-diffusivity as a function of temperature for the ideal gas. Do these equations provide the same temperature trends as the corresponding states chart in part (a)?

Based on kinetic theory, for the ideal gas, the shear viscosity, thermal conductivity and self-diffusivity increase with temperature.

(c) Are the trends with respect to temperature the same for shear viscosity, thermal conductivity and self-diffusivity of the *ideal gas*?

Yes, based either on kinetic theory or the corresponding states chart, all three properties increase with temperature in the ideal gas.

(d) What is the molecular basis for the trends observed in part (a)?

An increase in temperature corresponds to an increase in the mean velocity, which increases the frequency of collisions, which is the mechanism for momentum, heat and mass transfer in an ideal gas.

(e) Report the trends in shear viscosity, thermal conductivity and self-diffusivity as a function of temperature for the *liquid* based on the corresponding states chart, e.g. do these properties increase or decrease with temperature?

Based on the corresponding states chart, for the liquid, the shear viscosity and thermal conductivity decrease with temperature, while the self-diffusivity increases with temperature.

(f) Equation (1.5-11) on page 31, (9.4-3) on page 279 and (17.4-5) on page 529 provide estimates from a mixture of theory and empiricism on the temperature dependence of the shear viscosity, thermal conductivity and self-diffusivity as a function of temperature for the *liquid*. Do these equations provide the same temperature trends as the corresponding states chart in part (e)?

From equation (1.5.-11), the shear viscosity decreases with temperature, in agreement with the corresponding states chart. From equation (9.4.-3), the thermal conductivity is based on the velocity of sound, which is based on $\left(\frac{\partial p}{\partial \rho}\right)_T$. *A qualitative sketch of* $\left(\frac{\partial p}{\partial \rho}\right)_T$ *for the van der Waals equation of state, shows that* $\left(\frac{\partial p}{\partial \rho}\right)_T$ *is positive and decreases with temperature. Thus the thermal conductivity decreases with temperature, in agreement with the corresponding states* *chart. From equation (17.4-5), the self-diffusivity is proportional to* $\frac{T}{\mu}$. *Since from equation (1.5-11) we know that the viscosity decreases with T, we see that the net effect is an increase of the self-diffusivity with respect to temperature, in agreement with the corresponding states chart. Thus, these three empiricisms predict the same trends as the corresponding states chart.*

(g) Are all trends with respect to temperature the same for shear viscosity, thermal conductivity and self-diffusivity of the *liquid*?

No, based either on empiricisms or the corresponding states chart, the shear viscosity and thermal conductivity of a liquid decrease with temperature, whereas the self-diffusivity of a liquid increases with temperature.

(h) What is the molecular basis for the trends observed in part (e)?

An increase in temperature corresponds to an increase in the mean velocity, which increases the mobility of molecules. This enhanced mobility makes local structure (called cages in BSL2) more fluid, reducing friction between cages, lowering the viscosity. The enhanced mobility of molecules gives rise to higher self-diffusivities. At this point, I don't have a clear idea regarding the molecule-level mechanism that leads to the lowering of the thermal conductivity of a liquid as a function of temperature. At a non-molecular level, the thermal conductivity is proportional to the velocity of sound, which drops with increasing temperature. The molecular-level mechanism responsible for a drop in the velocity of sound in a material as a function of temperature…