Final Exam
ChE 548
Spring, 2006

Problem 1. Molecular Dynamics Simulation

Answer the following questions in terms of (i) the average particle velocity, (ii) the collision diameter, and (iii) the mean free path.

1.A. The Einstein relation for the self-diffusivity applies in the infinite time limit. At short times, a different kind of behavior is observed.

1.A.i. All other things being equal, will a simulation of a fluid at a high density or a low density approach the long-time behavior faster?

Answer: A simulation at a high density will approach the long-time behavior faster. We saw this in the practical application because we had to run gas simulations longer than liquid simulations. The reason for this is that the frequency of intermolecular collisions is based on the mean free path. As the density increases, the mean free path decreases. With a short mean free path, collisions become more frequent and the transition to the long-time behavior occurs more quickly.

1.A.ii. All other things being equal, will a simulation of a fluid at a high temperature or low temperature approach the long-time behavior faster?

Answer: A simulation at a high temperature will approach the long-time behavior faster. The reason for this is that the frequency of intermolecular collisions is also based on the average particle velocity. As the temperature increases, the average velocity increases. As a result, collisions become more frequent and the transition to the long-time behavior occurs more quickly.

1.A.iii. All other things being equal, will a simulation of a fluid at a high molecular weight or a low molecular weight approach the long-time behavior faster?

Answer: A simulation at a low molecular weight will approach the long-time behavior faster. Molecular weight does not affect mean free path. However, the molecular weight does effect the average velocity through the equipartition theorem. For a given temperature, a high mass results in a lower velocity. A lower velocity results in less frequent collisions. As a result, a higher mass leads to a longer approach to the long-time behavior.

1.B. Simulations have to undergo a period of "equilibration" during which time they forget their initial configurations (both position and velocities). After the system is equilibrated, then data production can begin. Answer the following questions.

1.B.i. Which will take longer: equilibration of the system or reaching the Einstein long-time limit? Why?

Answer: Generally speaking, one can obtain good average properties in shorter simulation than one can obtain good average transport properties. Thus, we can argue that the equilibration of the system occurs more quickly than reaching the Einstein long-time limit. The reason for this is that thermodynamic properties are instantaneous properties, whereas diffusivities (and other transport properties) are evaluated by tracking an auto-correlation function over time. In other words, there is no "instantaneous" diffusivities. These properties can only be evaluated over many time steps.

Problem 2. Macroscopic Material, Momentum and Energy Balances

Consider an inviscid, ideal gas flowing down a pipe with circular cross section. Consider only axial variation in properties. The pipe is insulated and there is no heat loss. The inlet conditions are

$$\rho(z=0)=\rho_{in} \tag{1}$$

$$v(z=0)=v_{in} \tag{2}$$

$$T(z=0)=T_{in} \tag{3}$$

The outlet condition is

$$\left.\frac{dT}{dz}\right|_{z=L}=T'_{out} \tag{4}$$

The general material, momentum, and energy balances are

$$\frac{\partial\rho}{\partial t}=-\nabla\cdot(\rho\mathbf{v}) \quad , \tag{5}$$

$$\rho\frac{\partial\mathbf{v}}{\partial t}=-\rho\mathbf{v}\cdot\nabla(\mathbf{v})-\nabla p-\nabla\cdot\boldsymbol{\tau}-\rho\nabla\hat{\Phi} \quad , \tag{6}$$

$$\frac{\partial\rho\left(\frac{1}{2}v^2+\hat{H}+\hat{\Phi}\right)}{\partial t}-\frac{\partial p}{\partial t}=-\nabla\cdot\rho\left(\frac{1}{2}v^2\cdot\mathbf{v}+\hat{H}\mathbf{v}+\hat{\Phi}\mathbf{v}\right)-\nabla\cdot\mathbf{q}-\nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v}) \quad , \tag{7}$$

Solve for the steady state profile.

Answer:
We make the following reductions in the balances. First, the system is at steady state, so all of the time derivatives disappear. Second, the viscosity is zero, so all of the viscous terms

disappear. Third, there is no external potential, so all of the Φ terms disappear. Fourth, it is one-dimensional, so all of the gradients become ordinary derivatives with respect to z.

$$0 = \frac{d\rho v}{dz} \quad , \tag{8}$$

$$0 = -\rho v \frac{dv}{dz} - \frac{dp}{dz} \quad , \tag{9}$$

$$0 = -\frac{d}{dz}\rho\left(\frac{1}{2}v^3 + \hat{H}v\right) - \frac{dq}{dz} \quad , \tag{10}$$

Fifth, we use the ideal gas approximations

$$p = \frac{\rho RT}{m} \quad , \tag{11}$$

$$H = C_p T \quad , \tag{12}$$

such that

$$\frac{dp}{dz} = \frac{RT}{m}\frac{d\rho}{dz} + \frac{\rho R}{m}\frac{dT}{dz} \quad , \tag{13}$$

$$\frac{dH}{dz} = C_p \frac{dT}{dz} \quad , \tag{14}$$

Sixth, we use Fourier's law

$$q = -k_c \frac{dT}{dz} \quad , \tag{15}$$

Substitute (11) through (15) into (8) through (10).

$$0 = \frac{d\rho v}{dz} \quad , \tag{16}$$

$$0 = -\rho v \frac{dv}{dz} - \frac{RT}{m}\frac{d\rho}{dz} - \frac{\rho R}{m}\frac{dT}{dz} \quad , \tag{17}$$

$$0 = -\frac{d}{dz}\rho\left(\frac{1}{2}v^3 + C_p T v\right) + k_c \frac{d^2 T}{dz^2} \quad , \tag{18}$$

Now simplify. The material balance becomes

$$\frac{d\rho}{dz} = -\frac{\rho}{v}\frac{dv}{dz} \quad , \tag{19}$$

Solve this

$$d\ln\rho = -d\ln v \quad , \tag{20}$$

Integrate.

$$\ln\left(\frac{\rho}{\rho_{in}}\right) = \ln\left(\frac{v_{in}}{v}\right) \quad , \tag{21}$$

Simplify.

$$\rho(z) = \frac{\rho_{in} v_{in}}{v(z)} \quad , \tag{22}$$

Substitute (19) and (22) into momentum and energy. The momentum balance becomes.

$$0 = \left(\frac{RT}{mv^2} - 1\right)\frac{dv}{dz} - \frac{R}{vm}\frac{dT}{dz} \quad , \tag{23}$$

Simplify

$$\left(\frac{T}{v} - \frac{vm}{R}\right)\frac{dv}{dz} = \frac{dT}{dz} \quad , \tag{24}$$

Now substitute equations (19), (22) and (24) into the energy balance (18). First expand the energy balance

$$0 = -\frac{1}{2}v^3\frac{d\rho}{dz} - \frac{3}{2}\rho v^2\frac{dv}{dz} - C_p T v\frac{d\rho}{dz} - C_p \rho T\frac{dv}{dz} - C_p \rho v\frac{dT}{dz} + k_c\frac{d^2T}{dz^2} \quad , \tag{25}$$

$$0 = \left(\frac{1}{2}v^3 + C_p T v\right)\frac{d\rho}{dz} + \rho_{in}v_{in}\left(\frac{3}{2}v + C_p\frac{T}{v}\right)\frac{dv}{dz} + C_p\rho_{in}v_{in}\frac{dT}{dz} - k_c\frac{d^2T}{dz^2} \quad , \tag{26}$$

$$0 = \rho_{in}v_{in}\left(-\frac{1}{2}v - \frac{C_pT}{v} + \frac{3}{2}v + \frac{C_pT}{v}\right)\frac{dv}{dz} + C_p\rho_{in}v_{in}\frac{dT}{dz} - k_c\frac{d^2T}{dz^2} \quad , \tag{27}$$

$$0 = \rho_{in} v_{in} v \frac{dv}{dz} + C_p \rho_{in} v_{in} \frac{dT}{dz} - k_c \frac{d^2T}{dz^2} \quad , \tag{28}$$

Now consider our current equations.

$$0 = \rho_{in} v_{in} v \frac{dv}{dz} + C_p \rho_{in} v_{in} \frac{dT}{dz} - k_c \frac{d^2T}{dz^2} \quad , \tag{28}$$

$$\frac{dv}{dz} = \frac{Rv}{RT - mv^2} \frac{dT}{dz} \quad , \tag{24}$$

Let’s eliminate the velocity derivative in the energy balance.

$$0 = \rho_{in} v_{in} \left(\frac{Rv^2}{RT - mv^2} + C_p \right) \frac{dT}{dz} - k_c \frac{d^2T}{dz^2} \quad , \tag{29}$$

It doesn’t look like there is much simplification here.

Now consider if the thermal conductivity is negligible. The energy balance becomes

$$0 = \rho_{in} v_{in} \left(\frac{Rv^2}{RT - mv^2} + C_p \right) \frac{dT}{dz} \quad , \tag{30}$$

$$0 = \frac{dT}{dz} \quad , \tag{31}$$

This means the temperature is constant.

$$T(z) = T_{in} \quad , \tag{32}$$

If the temperature is constant, then the velocity is constant from the momentum balance.