CE 530

Assignment #1 Solution

1. For this problem you will collect data from the discontinuous molecular dynamics applet at http://www.etomica.org/app/modules/sites/swmd/swmd2d.html.

(a) Navigate to this applet, and run it for two state points (different temperatures and/or densities) for the ideal-gas model. Evaluate the group Z = PA/NRT, and report your value. Be sure to include error estimates. Also, remember to reset the averages whenever you change the state parameters.

(b) Then change to the hard-sphere model. Evaluate Z for a range of densities, and plot your results, showing confidence limits on the values. Run one of the densities at two different temperatures, and include both points on your graph. Also include on the plot the empirical equation of state given by Wood:

$$\frac{PA}{NRT} = 1 + 1.81380\,\rho\,\frac{1 - 0.356780\rho + 0.021447\rho^2}{1 - 1.775171\rho + 0.787808\rho^2}$$

where $\hat{\rho} = \rho / \rho_0$, with ρ the number density *N/A*, and $\rho_0 = \frac{2}{d^2\sqrt{3}}$ is the close-packed density (*d* is the disk diameter).

See results in spreadsheet.

2. Derive the expression for the impulse given in Slide 9 of Lecture 2, using the momentum- and energy-conservation formulas that precede it.

The equation is $\Delta\vec{p} = \dfrac{2m_1 m_2}{m_1 + m_2}\dfrac{\vec{v}_{12}\cdot\vec{r}_{12}}{\sigma^2}\vec{r}_{12} = m_R\dfrac{\vec{v}_{12}\cdot\vec{r}_{12}}{\sigma^2}\vec{r}_{12}$

where m_R is the reduced mass. We begin by writing $\Delta\vec{p} = a\vec{r}_{12}$, where a is to be determined by conservation of energy. This form ensures that the force acts along the direction of the line joining the centers of the atoms.

Conservation of momentum and energy are written

$$\left.\begin{aligned}\vec{p}_1^{\,new} &= \vec{p}_1^{\,old} + \Delta\vec{p}\\ \vec{p}_2^{\,new} &= \vec{p}_2^{\,old} - \Delta\vec{p}\end{aligned}\right\}\text{conservation of momentum}$$

$$\frac{1}{m_1}\left|\vec{p}_1^{\,new}\right|^2 + \frac{1}{m_2}\left|\vec{p}_2^{\,new}\right|^2 = \frac{1}{m_1}\left|\vec{p}_1^{\,old}\right|^2 + \frac{1}{m_2}\left|\vec{p}_2^{\,old}\right|^2 \quad \text{conservation of energy}$$

combining these formulas gives us

$$\frac{1}{m_1}\left|\vec{p}_1^{old}+\Delta\vec{p}\right|^2+\frac{1}{m_2}\left|\vec{p}_2^{old}-\Delta\vec{p}\right|^2=\frac{1}{m_1}\left|\vec{p}_1^{old}\right|^2+\frac{1}{m_2}\left|\vec{p}_2^{old}\right|^2 \tag{1}$$

note that the square of the sum of vectors expands as follows

$$\left|\vec{p}+\Delta\vec{p}\right|^2=\left|\vec{p}\right|^2+2\vec{p}\cdot\Delta\vec{p}+\left|\Delta\vec{p}\right|^2$$

Substitution of this formula in (1) causes the $\left|p_i^{old}\right|^2$ terms to cancel. If we now put in the expression for $\Delta\mathbf{p}$ in terms of $\mathbf{r}_{12}$ we have

$$2\left(\mathbf{v}_1^{old}-\mathbf{v}_2^{old}\right)\cdot a\mathbf{r}_{12}+\tfrac{2}{m_R}\left|a\mathbf{r}_{12}\right|^2=0$$

which uses $\mathbf{v} = \mathbf{p}/m$ and the reduced mass $m_R=\frac{1}{2}\left(\frac{1}{m_1}+\frac{1}{m_2}\right)$. The scalar a can be divided out (the zero root corresponds to the spheres passing right through each other), and we note that at the collision $|\mathbf{r}_{12}|^2 = \sigma^2$. Then we conclude $a=m_R\dfrac{\mathbf{v}_{12}\cdot\mathbf{r}_{12}}{\sigma^2}$, which leads directly to the desired result.

3. Derive an expression for the (vector) impulse applied to two square-well atoms as they approach each other from outside their wells. Let the diameter of the wells be λ and the depth of the wells be ε.

The only change from the previous problem is that the energy conservation equation must also consider the change in potential energy that occurs when the two particles enter each other's wells. Before they "collide" their pair energy is zero, and after they collide their pair energy is $-\varepsilon$. Thus the energy conservation is

$$\frac{1}{2m_1}\left|\vec{p}_1^{old}+\Delta\vec{p}\right|^2+\frac{1}{2m_2}\left|\vec{p}_2^{old}-\Delta\vec{p}\right|^2-\varepsilon=\frac{1}{2m_1}\left|\vec{p}_1^{old}\right|^2+\frac{1}{2m_2}\left|\vec{p}_2^{old}\right|^2$$

Note that the new kinetic energy must be greater (assuming ε is positive), *i.e.*, the particles speed up upon their encounter. Proceeding as above

$$-\varepsilon-a\mathbf{v}_{12}\cdot\mathbf{r}_{12}+a^2\tfrac{1}{m_R}\left|\mathbf{r}_{12}\right|^2=0$$

This is a quadratic equation in *a* that does not simplify quite as easily as before. But it is of course still easy. The solution is

$$a = \frac{m_R}{2\lambda^2}\left[\mathbf{v}_{12}\cdot\mathbf{r}_{12} + \sqrt{(\mathbf{v}_{12}\cdot\mathbf{r}_{12})^2 + 4\varepsilon\lambda^2 / m_R}\right]$$

We want the (+) root here. The (–) root corresponds to a hard repulsive collision at the wells, rather than an attraction. What happens for ε = 0? (remember that $\mathbf{v}_{12}\cdot\mathbf{r}_{12} < 0$)

4. Surface tension has the units of dynes/cm. Develop a dimensionless surface tension variable using molecular constants for a Lennard-Jones fluid

Surface tension δ has dimensions of force/length, or energy/length^2. To make a dimensionless surface tension, we need to divide by the LJ energy, and multiply by the LJ diameter. Thus:

$$\delta^* = \delta\sigma^2 / \varepsilon$$

5. A Lennard-Jones simulation was performed at T* = 1.4 and ρ* = 0.8. The simulation produced a dimensionless pressure of 2.856 and a dimensionless internal energy of -5.612. To what physical conditions (in K and moles/L) do these state conditions correspond, and what are the corresponding values of the pressure and energy (in MPa and kJ/mol). Use parameter values for Argon (σ = 3.465 Angstroms, ε/k = 113.5 K).

Actual temperature: $T = T^* \times (\varepsilon / k) = 1.4 \times 113.5K = 158.9K$

Actual density:

$$\rho = \rho^* / \sigma^3 = 0.8 \times \frac{1}{(3.465\times 10^{-10} m)^3} \times \left(\frac{1}{6.022\times 10^{23}}\frac{\text{moles}}{\text{molecule}}\right)\left(\frac{1\text{m}^3}{1000\text{liters}}\right) = 31.9\frac{\text{moles}}{\text{liter}}$$

Actual pressure:

$$P = P^*(\varepsilon / k)(R / N_A) / \sigma^3 = 2.856\times 113.5\text{K}\left(\frac{8.314\text{m}^3\text{Pa/K-mol}}{6.022\times 23}\right)\frac{1}{(3.465\times 10^{-10} m)^3}\frac{1\text{MPa}}{10^6\text{Pa}} = 107.6\text{MPa}$$

Actual energy: $U = U^*(\varepsilon / k)(R) = -5.612 \times 113.5\text{K} \times 0.008314 \text{ kJ/K-mol} = -5.3 \text{ kJ/mol}$